



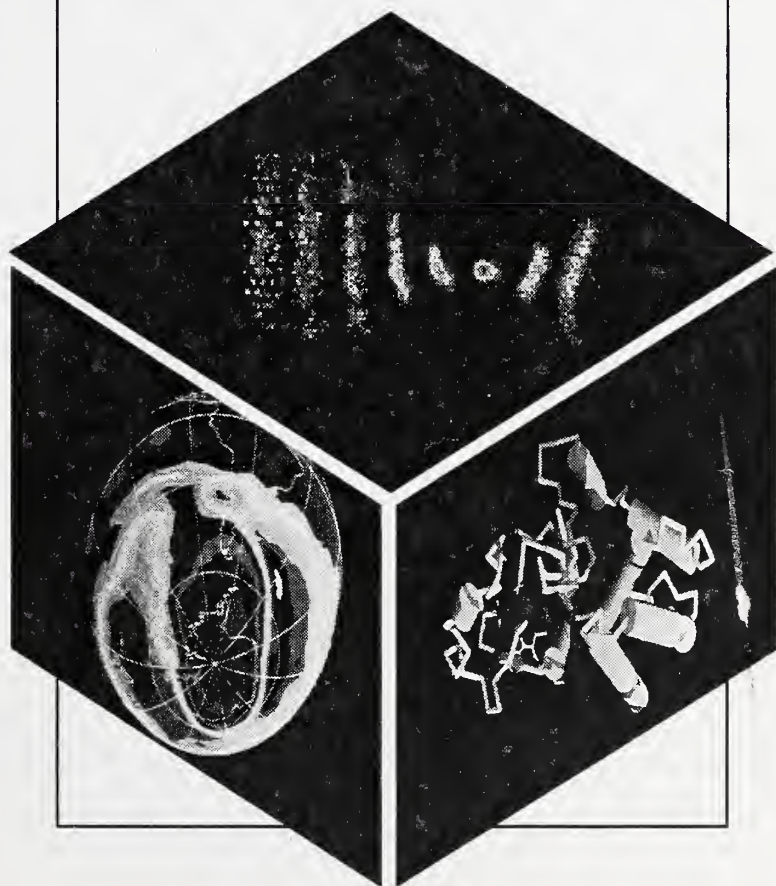
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NIST
PUBLICATIONS

NISTIR 5111

Chemical Science and
Technology Laboratory

CSTL Technical Activities 1992



U.S. DEPARTMENT OF COMMERCE

Technology Administration

National Institute of Standards and Technology

Submitted to the Board on Assessment of NIST Programs, National Research Council

May 25-26, 1993

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Shown on the cover (clockwise, starting at the top): images along the neutron beam path at the exit end of a prototype neutron focusing lens, taken with a video radiation detector developed at NIST; A monomer of the three-dimensional structure of Glutathione S-Transferase (GST), a human enzyme produced in the liver and other tissues, whose structure is being studied to help design more effective treatments for cancer; Depiction of stratospheric ozone showing the "hole" in the ozone layer in the region of the south pole. CSTL scientists provide physical and chemical data necessary to model the effects of man-made chemicals on the ozone layer.

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1993

Chemical Science and Technology Laboratory

1992 Technical Activities

Submitted to the Panel for
Chemical Science and Technology Laboratory
Board on Assessment of NIST Programs
National Research Council

May 25-26, 1993

Hratch G. Semerjian, Director
Chemical Science and Technology Laboratory
National Institute of Standards and Technology



U.S. DEPARTMENT OF COMMERCE, Ronald H. Brown, Secretary
National Institute of Standards and Technology, Raymond G. Kammer, Acting Director

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Chemical Science and Technology Laboratory

Hratch G. Semerjian, Director

Barry I. Diamondstone, Deputy Director

A. Program Overview

The expanded responsibilities we were given nearly five years ago in becoming the National Institute of Standards and Technology have provided us with a significant challenge. We were instructed to more directly couple our research with industrial needs in the United States, while continuing to provide: the national system of chemical and physical measurements, the fundamental research base for tomorrow's chemical science and technology, and a national reference laboratory to address critical problems related to public health and safety. With these goals in mind, the following comprehensive mission statement was written for the Chemical Science and Technology Laboratory:

- a) provide the national system of chemical and physical measurements; coordinate the system with measurement systems of other nations and furnish essential services leading to accurate and uniform chemical measurements throughout the Nation's scientific community, industry, and commerce; provide advisory and research services to other government agencies; conduct basic and applied research in analytical chemistry, biotechnology, chemical engineering, and physical chemistry; and conduct interdisciplinary research efforts with other NIST laboratories in these areas;
- b) conduct fundamental investigations of the phenomena on which measurement of the composition and behavior of chemical and biochemical systems is based; provide benchmark experimental data, new theory and models to explain the behavior and predict the properties of chemicals in chemical and biochemical processes and systems; develop and certify Standard Reference Materials; produce and evaluate Standard Reference Data; acquire and disseminate thermophysical, thermodynamic, kinetic, and thermal data; provide calibration services for temperature, pressure, vacuum, flow, volume, liquid density, and humidity; develop new laboratory and process measurement techniques, including in-situ real-time process measurement methods;
- c) aid competitiveness in the global marketplace of the diverse U.S. industries that are reliant on generic research and technology development in chemistry and chemical

NOTE: Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

engineering; develop and improve measurement capability and quantitative understanding of basic physical processes that underlie measurement science, including methods for analytical chemistry, biological chemistry, chemical kinetics, thermodynamics, and surface science, and thereby improve comparability among laboratories; use the methods to assist in the solution of problems of national impact, e.g., in improving the accuracy of clinical analytical chemistry, air and water pollution analysis, and chemical engineering metrology.

Our current activities address important areas within the mission of the Chemical Science and Technology Laboratory. Some indicators of success in meeting the expanded responsibilities of our new mission are Cooperative Research and Development Agreements (CRADAs), patents, research publications and talks, and measurement services such as Standard Reference Materials (SRMs), calibrations and Standard Reference Databases (SRDs). Accomplishments in FY92 are summarized in the table below.

Div.	Pubs.	Talks	Committees ¹	Seminars	Conferences	CRADAs	Patents	SRMs	SRDs	Cals. ²
830	8	7	19	9	4	0	0	0	0	0
831	84	80	51	34	2	3	4	2	1	0
832	17	17	16	0	0	0	4	0	1	3
833	49	59	50	8	2	0	0	3	5	0
834	95	116	109	17	9	7	1	112	0	156
835	46	36	34	19	3	5	0	48	0	0
836	77	85	77	18	11	3	4	3	0	1093
837	83	124	60	6	2	0	0	6	2	0
838	82	80	72	34	4	1	4	0	4	143
Totals	541	604	488	145	37	19	17	174	13	1395

¹Committee totals include 52 editorships

²Calibrations were performed for over 400 customers

There were many noteworthy accomplishments by CSTL personnel in these areas in FY92, some examples of which are presented below. More detailed information about these activities can be found in the writeups of the appropriate Divisions (indicated by the numbers in parentheses).

Research efforts by CSTL scientists in a number of diverse areas have been recognized by their colleagues. Among the outstanding achievements were the development of accurate and practical models for predicting thermodynamic properties of alternative refrigerants and refrigerant mixtures that was part of a comprehensive research program on alternate refrigerants (838); the structural characterization of the liver detoxification enzyme glutathione S-transferase (831); the breakthrough application of trace nanoanalysis to materials science problems such as the concentration and homogeneity of nitrogen in diamond, and rare earths in nanoscale yttrium oxide (837); the integration of ultrathin film and silicon micromachining technologies to develop a new generation of chemical sensing arrays (836); the construction of instrumentation for neutron depth profiling and for the focusing of neutrons (834); the application of flow injection

immunoassay technology for health and environmental uses (835); and the development of the first simple, conveniently applied schemes for the detection of ground state methylene radicals in combustion sources (833).

More than 500 *publications* were authored or coauthored by CSTL scientists and about 600 *talks* were presented at local, national and international meetings. Two manuscripts from CSTL were nominated for the Condon Award which recognizes distinguished achievement in written exposition in science or technology. A comprehensive study and review of the characteristics and measurement of atmospheric particles was published (837). A special issue of the journal *Spectrochimica Acta* focusing on Reference Materials and Reference Methods was edited and written by CSTL personnel (834) in collaboration with scientists from the U.S., Europe and Japan. The results of an international effort coordinated by NIST to standardize temperature measurements (836) was presented at the Seventh International Symposium on Temperature, where 23 separate publications were authored or coauthored by CSTL scientists. CSTL authors received the Algie Lance Award for the best paper at the 1992 Measurement Science Conference (836) and most outstanding paper on a 1-D Gel at the 1992 Electrophoresis Society Meeting (831).

A new government/industry consortium on Advanced Biosensors (831) was established to address generic problems and foster biosensor development and commercialization. *CRADAs* in this area are currently under development with 20-30 companies. A collaborative program in the development of microwave-assisted sample preparation technology for trace organic analysis (835) will result in more time and reagent-efficient methods for food/nutrition and environmental analyses. A CRADA with one of the major manufacturers of pressure gauges (838) may lead to a new type of primary pressure standard in the important range near atmospheric pressure. The Consortium for Automated Analytical Laboratory Systems (CAALS) will be producing its first standard in communication protocol between analytical system components (834). Research was initiated in collaboration with industry to develop a 10 K refrigerator for superconducting microelectronic circuitry (832).

Patents were awarded to CSTL scientists for a diffraction device to detect the Bragg Condition (837), an apparatus and method for evaporative sample concentration (838), a system for detecting transition and rare earth elements in a matrix (834), a method for making single crystals (832), the manufacture and use of a composite membrane for separating azeotropic or close-boiling mixtures (832), and a new method for aqueous two-phase protein extraction (832). Among the other 12 pending patent applications from CSTL were a desktop spectrum analyzer (837), novel developments in thermocouples and chemical sensors (836), and unique applications of biotechnology (831).

SRMs, calibrations, and SRDs remain a high priority in CSTL. Over 170 *SRMs* were certified for chemical composition or physical properties. Examples of important work in this area include the development of an SRM for the quality assurance of forensic DNA profiling measurements (831), certification of SRMs for asbestos (837), preparation of a lead paint film

SRM for calibration of portable X-ray fluorescence instruments (834), preparation of a highly-accurate rhodium solution SRM that will solve a multi-million dollar industrial problem (834), development of gas mixture SRMs for environmental monitoring (835) and certification of new SRMs for organic contaminants in whale blubber and marine sediment (835) and inorganic constituents in a series of three soil SRMs (834) that will provide for significant improvement in the characterization of environmental pollutants. Important *calibration* services continue in the areas such as airspeed, fluid flowrate, humidity, liquid density, temperature, and volume measurements (836), optical filter transmission for absorption spectrophotometers (834), and pressure and leak rate measurements (838). A number of significant *SRDs* were issued including a new vapor-phase infrared database of 5,500 FT-IR spectra, a new database of spectroscopic properties of atoms and atomic ions, and updates of the NIST Chemical Kinetics database and the NIST/EPA/MSDC Mass Spectral database (833). CSTL research on alternative refrigerants is disseminated through a computer program/database (REFPROP) that provides information of thermophysical properties and has been adopted as a standard by the air conditioning and refrigeration industry (838).

Several CSTL scientists received *awards* and recognition for outstanding achievements in FY92. These included presentation of the Department of Commerce Gold Medal to W. May, Silver Medal to L. Powell and G. Rosasco, and Bronze Medal to R. Parris, M. Schantz, W. Bowers and C. Ehrlich; the Outstanding Commerce Volunteer Award to M. Kline; the NIST Applied Research Award to G. Morrison and M. McLinden; the NIST Measurement Services Award to D. Reeder, K. Richie, L. Sniegowski, P. Huang, M. Huber, P. Looney and G. Morrison; and the Arthur Flemming Award (sponsored by the Office of Personnel Management) for Outstanding Federal Government Service to E. Steel. External awards to CSTL scientists included election of J.M.H. Levelt Sengers to the National Academy of Engineering and W. Egelhoff as a Fellow of the American Physical Society; the Humboldt Research Award for senior U.S. scientists to H. Hanley; the Percy Julian Award of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers to W. May; the Henry Storch Award in Fuel Chemistry of the American Chemical Society to S. Stein; and the Riviere Prize of the UK ESCA Users Group to C. Powell. J.M.H. Levelt Sengers and J.V. Sengers received honorary doctorates from the Technical University of Delft, The Netherlands for their outstanding research and leadership in the area of thermophysics.

Several major *conferences and workshops* were organized or coorganized by CSTL scientists in FY92. The Seventh International Symposium on Temperature: Its Measurement and Control in Science and Industry was held in April 1992, and is the definitive forum for establishing temperature measurement capabilities throughout the world. Our staff also participated in the organization of ECOWORLD'92.

As this overview indicates, we strive to achieve a balance between providing essential measurements and technology, and carrying out basic research to ensure a healthy science and technology base for the future. Each Division in CSTL is responsible for basic and applied

research, and for maintaining close contacts with appropriate scientific and industrial communities.

In the following pages, recent activities, technical directions and outputs of the CSTL Divisions are highlighted.

B. Outputs and Interactions
(Chemical Science and Technology Laboratory)

1. Publications

Presser, C., Gupta, A.K., Avedisian, C.T. and Semerjian, H.G., "Combustion of Methanol and Methanol/dodecanol Spray Flames," J. Propulsion and Power, 8, 553-559 (1992).

Presser, C., Gupta, A.K., and Semerjian, H.G., "Aerodynamic Effects on Fuel Spray Characteristics: Pressure-jet Atomizer," Combustion & Flame, 92, 25-44 (1993).

Fairfield, M.S., Butler, T.D., Presser, C., Gupta, A.K., and Semerjian, H.G., "Aerodynamic Effects on Fuel Spray Structure - Experiment and Theory," AIAA Paper No. 92-0227, 30th AIAA Aerospace Sciences Meeting, Reno, NV (January 1992).

McAvoy, T.J., Su, H.T., Wang, N.S., He, M., Horvath, J.J., and Semerjian, H.G., "A Comparison of Neural Networks and Partial Least Squares for Deconvoluting Fluorescence Spectra," Bioengineering and Biotechnology, 40, 53-62 (1992).

Avedisian, C.T., Presser, C., Gupta, A.K., and Semerjian, H.G., "Observations of Soot in Combustion of Methanol/Toluene Spray Flames," Proc. ASME Winter Annual Meeting, Anaheim, CA (1992).

Zurlo, J.R., Presser, C. and Semerjian, H.G., "Estimation of Droplet Collision Frequency in a Spray," Proc. 5th Ann. Conf. on Liquid Atomization and Spray Systems (ILASS Americas'92), pp. 97-101, San Ramon, CA (May 1992).

Hodges, J.T., Grehan, G., Presser, C. and Semerjian, H.G., "Elastic scattering from spheres under non plane-wave illumination," SPIE Proceedings, 1862, No. 33 (1993).

Becker, D., Christensen, R., Currie, L., Diamondstone, B., Eberhardt, K., Gills, T., Hertz, H., Klouda, G., Moody, J., Parris, R., Schaffer, R., Steel, E., Taylor, J., Watters, R., and Zeisler, R., "Use of NIST Standard Reference Materials for Decisions on Performance of Analytical Chemical Methods and Laboratories," NIST Special Publication 829, 1992.

2. Talks

Diamondstone, B.I., "Accuracy and Quality Assurance at NIST," SAC 92 & 150th Anniversary of the Laboratory of the Government Chemist, Univ. of Reading, Reading, UK, September 25, 1992.

Hertz, H.S., "Accuracy and Quality Assurance in the Analytical Laboratory," Analytical Laboratory Managers Association, NIST Gaithersburg, MD, October 23, 1991.

Hertz, H.S., "Accuracy and Quality Assurance at NIST," 12th Annual ALMA Meeting, Gaithersburg, MD, October 24-25, 1991.

Hertz, H.S., "What Federal Agencies Can Do," Pipeline for Women and Minorities in the Chemical Sciences, PITTCO Conf., New Orleans, LA, March 9-13, 1992.

Semerjian, H.G., "Measurements in Spray Combustion Systems," Rutgers University, Piscataway, NJ, October 30, 1991.

Semerjian, H.G., "Structure of Spray Flames," University of California-at Berkeley, Berkeley, CA, November 15, 1991.

Semerjian, H.G., "Environmental Technologies at NIST," Environmental Tech Transfer '92, Crystal City, VA, November 10, 1992.

3. Committee Assignments

B.I. Diamondstone

American Chemical Society Committee on Chemical and Public Affairs
Subcommittee on Research and Science Policy
ASTM Committee D34, Hazardous Wastes
ASTM Committee E-01, Chemical Analysis of Metals
ASTM Committee E01.01, Ferrous Metals
ASTM Committee E01.20, Fundamental Practices (Secretary)
Analytical Laboratory Managers Association (President)
Council for Chemical Research
Directors of Industrial Research - Analytical Group

H.G. Semerjian

Combustion Institute - 24th Symposium (International) on Combustion, Program Subcommittee
ASME K-11 Committee on Heat Transfer in Fires and Combustion Systems

AIChE Engineering Sciences and Fundamentals Group, Area 1b. - Kinetics, Catalysis and Reaction Engineering
AIChE Food, Pharmaceutical and Bioengineering Division, Area 15C - Biotechnology
International Conference on Liquid Atomization and Spray Systems
ICLASS-91 - Conference Chairman
ICLASS-94 - Organizing Committee
ECOWORLD'92, Advisory Board
Council for Chemical Research - Subcommittee on Science Education
Directors of Industrial Research - Analytical Group

4. Editorship

H.G. Semerjian

Combustion Science and Technology, Vol. 82, Special Issue on Fundamental Processes in Combustion, Incineration and Reaction Engineering, Guest Editor.

5. Laboratory Colloquium Series

October 9, 1991

John Tully, AT&T Bell Laboratory, Murry Hill, NJ, Chemical Dynamics at Metal Surfaces.

December 18, 1992

C.A.M. Brenninkmeijer, Department of Scientific and Industrial Research, New Zealand, ^{14}C , ^{13}C and ^{18}O Measurements of Atmospheric Carbon Monoxide in New Zealand, Europe and Antarctica.

January 8, 1992

William J. Taraszewski, Bristol-Meyers Squibb Company, Evansville, IL, Drug Development and Approval: The Role of Analytical Chemistry.

February 13, 1992

William H. Zoller, University of Washington, Seattle, WA, Aerosol Chemistry in Hawaii: 1979-1991.

March 4, 1992

Walter W. Stewart and Ned Feder, NIH, Bethesda, MD, The Baltimore Fiasco: A Case Study in Fraud.

April 22, 1992

Adrian Wade, Univ. British Columbia, Canada, Chemical Acoustic Emission: Can Chemical Reactions Talk Intelligibly?.

May 20, 1992

Graham Morrison, NIST, Picking Apples in a Shrinking Orchard: Are There New Orchards? The Search for Alternative Refrigerants.

June 15, 1992

Ernie Baughman, Amoco, and Bruce Kowalski, Center for Process Analytical Chemistry, Process Analytical Chemistry: Standards and Standardization.

August 12, 1992

Derek J. Gardiner, University of Northumbria at Newcastle, England, Advanced Micro-Raman Instrumentation for Materials Research.

6. Conferences/Workshops Sponsored/Co-Sponsored

November 17-22, 1991

Combustion Reaction Engineering Session, American Institute of Chemical Engineers (AIChE), 1991 Annual Meeting, Los Angeles, CA.

June 14-17, 1992

ECOWORLD'92, American Society of Mechanical Engineers, Washington, DC

October 21-23, 1992

13th Annual Meeting of the Analytical Laboratory Managers Association (ALMA), New Orleans, LA.

November 1-6, 1992

Combustion Reacting Engineering, American Institute of Chemical Engineers (AIChE), 1992 Annual Meeting, Miami Beach, FL.

I. Biotechnology Division (831)

Lura J. Powell, Chief

A. Division Overview

The NIST Biotechnology Division was created as a part of an agency-wide reorganization in February 1991. Scientists from seven technical divisions were brought together to form the new Division which brings to fruition an effort begun in the mid-1980's to establish a major new NIST effort to develop the generic measurements, models, data and standards needed to accelerate the commercialization of biotechnology in the United States.

At the behest of the U.S. Senate, NIST prepared a plan for a national effort to develop measurements and standards for biotechnology. The plan recognized that commercialization of biotechnology will be measurement intensive with an estimated cost of up to 25 percent added to the products of biotechnology for such measurements. Measurements are vital in each developmental stage of a biochemical product--in the research laboratory, in the proof of process and process equipment scale-up in pilot plants, in commercial scale production, and in assuring that products meet or exceed market standards and customer specifications. These measurements are primarily chemical and physical in nature.

The Biotechnology Division provides NIST with a cohesive biotechnology effort focused on the most critical measurement needs of the biotechnology industry, fosters collaboration among NIST scientists conducting biotechnology research, and raises the visibility of NIST contributions to biotechnology research, standards and data leading to collaborations with industry, universities and other government agencies. During FY92, the Division has been involved in a number of activities which will assist the private sector in commercializing biotechnology research. Contacts were established with the two primary Biotechnology trade organizations, the Association of Biotechnology Companies (ABC) and the Industrial Biotechnology Association, and the Division has become a member of the ABC. The Division is taking an active role in ASTM Committee E-48 on Biotechnology and planning is underway for a major workshop in April, 1993 to assess and prioritize Biotechnology standardization needs. A Consortium on Advanced Biosensors (CAB) was planned and initiated to address the priority research needs of biosensor industry. The Division certified the first NIST Biotechnology Standard Reference Material, a DNA profiling quality assurance kit which will be used to assure the accuracy of DNA measurements in forensic and paternity testing. The Division was also actively involved in a number of other collaborations with industry including Cooperative Research and Development Agreements (CRADAs) with IBM and ICN Biomedicals.

The Biotechnology Division played a major role in the Biotechnology Research Subcommittee (BRS) of the Federal Coordinating Committee on Science, Engineering, and Technology (FCCSET) Committee on Life Science and Health. The BRS has the long-term charge of coordinating biotechnology research throughout the Federal government and providing

recommendations on areas of opportunity for the future. Biotechnology was chosen as a Presidential Initiative for FY93. The BRS was given responsibility for developing the report, "Biotechnology in the 21st Century" which includes priority recommendations for biotechnology research which fit very well with NIST priorities for its Biotechnology program. NIST Biotechnology Division staff were chosen to Chair the Bioprocessing and Technology Transfer Working Groups. Other staff members served on the Structural Biology, Health, General Foundations and Infrastructure Working Groups. As a result of this involvement, NIST biotechnology research, while representing only 0.1% of the total Federal investment in biotechnology research, is well represented in the BRS report and its recommendations, and collaborations with other agencies have resulted.

The Division participated in a National Research Council study on Bioprocess Engineering. The report resulting from this study, "Putting Biotechnology to Work: Bioprocess Engineering" was completed in August, 1992. It will be very useful in Division long range planning efforts and in justifying our Bioprocess Engineering programs during the budget process.

The mission of the NIST biotechnology program is to advance the commercialization of biotechnology by developing the scientific/engineering technical base, reliable measurement techniques and data to enable U.S. industry to quickly and economically produce biochemical products with appropriate quality control. As with all NIST programs, a major emphasis of the NIST biotechnology program is to provide advisory and research services to industry, other government agencies and the scientific community. The Division was reorganized in April, 1992 to include a Biosensor Technology Group, since this technology was chosen as a focus area for the Division. The new Group structure of the Biotechnology Division follows: (1) Biochemical Measurements whose activities are focused on separation, modification, immobilization and stabilization of biomolecules and mechanisms of DNA damage and repair; (2) Biophysical Measurements, whose activities focus on biothermodynamics and transport processes of biomolecules; (3) Center for Advanced Research in Biotechnology (CARB), whose activities focus on the understanding of protein structure/function and energetics (CARB is a joint venture with the University of Maryland and Montgomery County, Maryland); and (4) Biosensor Technology whose activities focus on development of advanced biosensing devices and biomolecular electronics.

The primary research efforts of the Biotechnology Division are focused on the following areas:

DNA and Protein Chemistry/ Standards Development

DNA Profiling: Methods and standards are being developed to accurately characterize DNA profiles for forensic and other uses. A standard reference material for quality control and standardization of forensic DNA testing was completed in August, 1992. Research is being conducted to develop the next generation of DNA profiling based on polymerase chain reaction technology including new methods development for rapid DNA extraction, amplification, separation, and computer imaging.

DNA Damage and Repair: Methods have been developed to characterize DNA damage on a molecular scale using GC/MS techniques. Studies of both *in-vivo* and *in-vitro* systems are underway to understand both damage (as low as one base per million) and repair mechanisms.

Protein Mapping: 2-D electrophoresis, computer imaging and computational techniques are being applied to mapping of proteins in complex systems, including those of living tissues subjected to disease and treatments.

Bioprocess Engineering

Separation and Purification: Methodologies and the data necessary for their evaluation are being developed to affect the efficient separation and purification of products from their mother liquors.

Design Properties: Thermophysical, thermochemical and engineering properties are being obtained, evaluated, codified and modeled for ubiquitous biochemicals, biosystems and protein solutions of interest to biotechnology. These data will be used by the bioengineer to both optimize existing processes and to evaluate proposed processes.

Biosensor Technologies

Sensor Technologies: NIST develops generic sensor technologies utilizing both optical and electrochemical approaches for applications in clinical laboratories, bioprocessing and environmental monitoring.

Biomolecular Electronics: The light-sensitive protein, bacteriorhodopsin is being studied as a potential source for the storage and retrieval of information. This protein, when exposed to light, changes color, representing a change in transition state and storage or release of a byte of information. Studies are underway to understand the mechanism of this change in transition state and to develop methods of immobilizing this protein to increase its stability.

Consortium for Advanced Biosensors (CAB): The Consortium was formed to solving generic problems which prevent the commercialization of many biosensor technologies. The studies proposed for the Consortium, which will be conducted at NIST, are of an interdisciplinary nature and are such that most industrial companies do not have the instrumentation and expertise to carry them out. The research programs are chosen by the Consortium members and supported through yearly membership fees.

Protein Engineering (Structural Biology)

Structure/Function/Energetics Relationships: NIST is actively working to understand these relationships using the methods of protein crystallography, molecular biology, biothermodynamics, and computational chemistry and modeling.

Protein Crystallography: Active programs are underway to obtain the protein structure, using X-ray and NMR techniques of prototypical proteins, enzymes, enzyme-substrate complexes and model DNA systems. Other efforts include the development of a machine readable database for protein crystallization and the development of artificial intelligence techniques for interfacing laboratory robots for protein crystallization studies with the database.

Protein Folding: Computational and experimental methods have been developed to determine the thermodynamics, cooperativity and other parameters describing the energetics of protein folding.

Computational Chemistry and Modeling: Quantum mechanical formalisms involving reaction fields are being developed to model the energetics and dynamics of interactions between substrates and active sites of enzymes. Modeling techniques to understand the relationship between protein sequence and structure are being developed.

Several Division staff members received awards over the past year. Ms. M. Kline received the Department of Commerce Outstanding Volunteer Award for establishing emergency rescue services in her community of Smithburg, Maryland. Ms. Kline also received an award for most outstanding 1-D Gel at the Electrophoresis Society Meeting in June, 1992. Two members of the Division, Dr. D. Reeder and Ms. K. Richie were selected to receive a joint Measurement Services Award for the development and certification of the first biotechnology Standard Reference Material, SRM 2390, DNA Profiling Standard. Dr. L. Powell received a Department of Commerce Silver Medal for outstanding contributions to a coordinated national biotechnology research effort focused on measurement needs of the scientific community.

Future Directions

Future thrusts of the Biotechnology Division program include expanded efforts in structural biology, DNA separations bioprocess engineering, DNA separations and standards development, and new programs in biomolecular electronics, biomimetic chemistry and the spectroscopic studies of biomolecular systems. Plans have been developed for program expansions in biosensor technology, upstream and downstream bioprocessing, quality assurance of biotechnology measurements, and protein engineering technology. In addition plans were developed for a major NIST-wide NMR facility. These plans fit well with the recommendations of the Presidential Initiative in Biotechnology.

The current CARB facility is filled to capacity and plans are underway for expansion in cooperation with the University of Maryland. The present CARB facility is 38,000 square feet, which includes 18,000 square feet of research space and 20,000 square feet of conference facility and office/administrative space. A major expansion, CARB-II (100,000 square feet), will be initiated in 1996. An interim expansion, CARB-IB (20,000 square feet), will provide laboratory and office space for 10 additional tenure-track faculty. The design phase of this expansion is underway and occupancy is expected in late 1994. Proposed areas of research for CARB-IB include a Center for Excellence in Computational Biotechnology, synthetic and peptide chemistry, and enzymology.

**B. Selected Technical Reports
(Biotechnology Division)**

1. Physical Characterization of Heparin by Light Scattering

D.H. Atha, J.B. Hubbard, and A.K. Gaigalas

A Standard Reference Material which can be used to provide physical characterization of heparin is under development. Heparin is a sulfated polysaccharide often used as an effective antithrombotic agent. Its clinical use requires rigorous characterization to maintain uniformity in preparation. To extend this characterization, we have used quasielastic and electrophoretic light scattering to measure the size and charge heterogeneity. For porcine mucosal heparin ($M_r = 10\text{-}20$ kDa) we found the diffusion coefficient to be $1\text{-}2 \times 10^{-8}$ cm²/s and the mobility to be 4.4×10^{-4} cm²/Vs for an unfiltered solution in distilled water. This diffusion constant is about 100 times slower than expected for a molecule the size of heparin. A fast diffusion component of 6.8×10^{-7} cm²/s, corresponding to the individual molecule, was measured in the presence of 2 M NaCl, where single molecule motion is better observed. This shows that a portion of the heparin population is in an aggregated state and has a much higher scattering intensity than individual heparin molecules. The weight percentage of the aggregates was 5 to 10 percent as measured by high performance liquid chromatography. These aggregates are stable up to a temperature of 75 °C, as measured by light scattering. Using the diffusion coefficients, we estimate the average aggregate to be made up of about 70 heparin monomers. Using the mobility measurements, we estimate the charge on the aggregate to be about 1200 electron charges, or about 17 charges for each heparin monomer. The electrophoretic light scattering measurements also show that the aggregate scattering species have very similar surface charge densities. This would result from the aggregates being formed from heparin molecules.

2. Thermodynamic Analysis of the Carboxy-Terminal Heparin Binding Region of Fibronectin

D.H. Atha, F.P. Schwarz, V. Novokhatny (American Red Cross), and K. Ingham (American Red Cross)

Fibronectin is a large, multifunctional plasma protein that plays a key role in cell surface interactions. During the past year we investigated protein-carbohydrate interactions that take place in the heparin binding (hep-2) region of fibronectin. We have analyzed the domain structures and stabilities of fragments isolated from the hep-2 regions of fibronectin by differential scanning calorimetry (DSC) and fluorescence spectroscopy. The 30 kDa hep-2A fragment, obtained from the heavy chain, contains three type III modules (III₁₂ through III₁₄) whereas the 40 kDa hep-2B fragment contains four such modules (III₁₂ through III₁₅). Thermal unfolding of these fragments results in a large red shift in the fluorescence of the highly conserved, and at least partially buried, single tryptophans present in each module. This process

is irreversible at a neutral pH where the melting is highly cooperative, thus suggesting interactions between modules. DSC measurements in 50 mM glycine at pH 2.7 reveal the presence of three, independently-folded domains in the 30 kDa hep-2A, and four in the 40 kDa hep-2B. At neutral pH in the presence of denaturants, the endotherms obtained with the 30 kDa hep-2A became sharper than at pH 2.7, and only two transitions could be resolved. The larger of these transitions is stabilized by addition of heparin and, therefore, was assigned to modules III₁₃ and III₁₄ since these are known to be involved in heparin binding. We conclude that all type III modules in the hep-2 region of fibronectin are independently folded. In addition, these modules interact to form a highly cooperative structure at neutral pH through interactions that can be disrupted with acid, urea or guanidine hydrochloride.

3. Characterization of Soybeans (*Glycine max*) Using Two-Dimensional Electrophoresis and Size Exclusion Chromatography

K.D. Cole and J.J. Edwards

The nutritional properties of soybeans as both a human and animal food source is significant since, in addition to oil and fiber, soybeans contain about 35-40% protein by dry weight. Also, soybeans contain certain phytochemicals thought to have potent medicinal properties. Quantities of these components are different with each germline and cultivar. The usefulness of soy protein as a human food source is limited by certain antinutritional components such as the trypsin-class protease inhibitors that inhibit mammalian pancreatic serine proteinases. Differences in nutritional quality of many soybean germ lines are determined by the relative quantity of these protease inhibitors found in the seeds. In the medical field, especially in chemoprevention studies, protein and phytochemical constituents of soybeans are being tested for effects on tumorigenesis, oncogene suppression, and modulation of known carcinogen action.

Characterized biological constituents (proteins and isoflavones) of selected germ lines of soybeans are used in the production of both human and animal foods. A compilation of biological and chemical parameters will be useful to growers and manufacturers of soybeans. These parameters could help in the selection of optimal germ lines for planting, for assessing nutritional value, and for the quantification of potential medicinal components present in soybeans.

High-resolution one- and two-dimensional gel electrophoresis, modified staining protocols, and computerized image analysis were used to study the soy protein components. Over 400 individual protein components in each gel map were resolved and quantified, and proteins that are unique to particular germ lines were identified. Although the functions of these unique proteins are not known now, these techniques are being used for protein purification so that amino acid sequencing can be done. Some of these proteins possibly represent stress proteins that may have effects on plant growth characteristics, nutritional value and medicinal properties.

Using size exclusion chromatography of ethanol extracts of soybeans, a group of phenolic compounds called isoflavone glucosides, which are known to be of interest in various areas of cancer research, were isolated. Various isoflavones in selected germplines are currently being quantified, and a search for new isoflavone forms is underway. *In vitro* experiments are being conducted by researchers at the John Wayne Institute for Cancer Treatment and Research (Santa Monica, CA) who are testing the growth inhibiting effects of these isoflavones, as well as other soybean-derived protein components, on colon and gastric cancer cells.

4. Measurement of Typical Free Radical-Induced DNA Modifications in Chromatin of Human Cancerous Tissues and Their Cancer-Free Surrounding Tissues

M.M. Dizdaroglu and Z. Nackerdien (Univ. of Stellenbosch, South Africa)

Free radical-induced damage to DNA *in vivo* is implicated in playing a role in carcinogenesis. Evidence exists that DNA damage by endogenous free radicals occurs *in vivo*, and there is a steady-state level of free radical-modified bases in cellular DNA. Endogenous levels of typical, free radical-induced DNA base modifications were investigated in chromatin of various human cancerous tissues and their cancer-free surrounding tissues. Five different types of surgically removed tissues were used, namely colon, stomach, ovary, brain and lung tissues. In chromatin samples isolated from these tissues, five pyrimidine-derived and six purine-derived modified DNA bases were identified and quantified by gas chromatography/mass spectrometry. The identified compounds are known to be formed typically by hydroxyl radical attack on DNA bases. In all cases, elevated amounts of modified DNA bases were found in cancerous tissues. The amounts of modified bases depended on the tissue type. Lung tissues removed from smokers had the highest increases of modified bases above the control levels, and the highest overall amounts. Colon cancer tissue samples had the lowest increases of modified bases over the control levels. Some of these modified DNA bases are known to be promutagenic, although others have not been investigated for their mutagenicity. Identified DNA lesions may play a causative role in carcinogenesis and/or their high levels may be in part a result of the disease. Whatever the reason for this phenomenon, high levels of modified bases may contribute to the genetic instability of tumor cells, and thus to increased metastatic potential.

During the past year, the induction of DNA base damage and DNA-protein cross-links in chromatin of γ -irradiated or H_2O_2 -treated cultured human cells has been documented. Eleven modified bases were identified and quantified. The radiation yields of a number of modified bases were increased significantly over their background levels at a dose as low as 47 Gray. Hydroxyl radical involvement in product formation was inferred from the pattern of lesions, although their induction in part by the direct effect of ionizing radiation, through ionization of DNA bases, cannot be excluded. The yields of guanine-derived lesions amounted to $\approx 45\%$ of the total net yield of modified bases, followed by almost equal yields of adenine-, cytosine- and thymine-derived bases. The yields of modified bases were lower than those previously measured after γ -irradiation of fully expanded chromatin in aqueous buffer solutions.

5. Quality Assurance of DNA Profiling Measurements

K.L. Richie, M.C. Kline, and D.J. Reeder

DNA profiling, also known as DNA fingerprinting, is used to compare the DNA found at a crime scene with the DNA pattern of criminal suspects. It also can be used to establish paternity and to identify victims of mass disasters. The results of the profiling techniques are being accepted in criminal and civil court proceedings. The call by many groups for material standards has been met with the issuance of SRM 2390, DNA Profiling Standard. This SRM is the first SRM certified by the Biotechnology Division. SRM 2390 is composed of well-characterized human DNA in three forms, from a female cell line and from a male source. The set also contains DNA to be used for quantitative controls. For DNA band size determinations, a DNA ladder is included. A total of 20 components are included as a quality assurance set for the standard Restriction Fragment Length Polymorphism (RFLP) methods, or modifications thereof, used by the Federal Bureau of Investigation. Sample sets were analyzed using RFLP protocols at NIST and at 28 collaborating laboratories. Participating laboratories were asked to provide calculated band sizes for various DNA probes. Additionally, we obtained information about the procedures and variables associated with interlaboratory measurements. Extensive statistical studies allowed assignment of DNA band sizes for the SRM certificate. Additional statistical studies on the effects of many procedural variables are in process.

The Armed Forces DNA Identification Laboratory (AFDIL) is a newly-established group whose mission is to collect blood samples from all members of the Armed Services for archival purposes. These blood samples may be used for body identification by DNA methods in times of war or mass disasters. As part of a quality assurance exercise, the Biochemical Measurements group was asked to examine the collection matrix, a custom-prepared paper, for any DNA contamination that could ultimately confuse results.

The manufacturer of the paper (SS 903) sent 10 coded samples taken from various stages of manufacturing process. These samples, three of which had liquid components, were tested for the presence of endogenous DNA that could be amplified by the polymerase chain reaction (PCR) process and could therefore interfere with typing results. Results of these studies showed that no DNA was present. For control purposes, a sample of the SS 903 paper was spotted with blood and subsequently extracted in the same manner as the blank papers. The DNA recovered from this control was typed correctly.

Tests were also performed to assess the quantity and the quality of the DNA recovered from blood stained SS 903 paper using three different DNA extraction procedures. Additionally, tests were conducted to determine whether the location from which the sample is taken (outer, middle, or inner region) has an effect on the results. Small samples were punched from several blood stains and extracted for DNA. Results showed that a Chelex 100 extraction procedure produced a sufficient amount of DNA for typing, while the currently used organic or non-organic

extraction procedures only furnished minimal amounts of DNA. Only the Chelex-extracted samples were usable in the DNA typing processes.

6. **Structural Studies of an Immunogenic Small Protein Component of HIV-1 Coat Glycoprotein GP120 by High Field Proton NMR Spectroscopy**

B. Coxon, K. Gawrisch (NIH), J. A. Ferretti (NIH), J. Blomberg (Lund Univ., Sweden), and R. Pipkorn (Lund Univ., Sweden)

The biological strain variability and immunogenic specificity of the HIV-1 virus are known to involve the amino acid sequence and/or structure of a region of the coat glycoprotein known as the third hypervariable (v3) loop. As part of a program to study the binding of human antibodies with the principal neutralizing determinant in the v3 loop, we have studied the solution structure of a small protein component of the coat glycoprotein GP120 of the JY1 (African) strain by high field proton NMR spectroscopy and circular dichroism.

This protein component contains 35 amino acids (molecular weight $\approx 4,000$) and was prepared by solid-phase synthesis, according to the known genome of HIV-1. The protein was then oxidatively cyclized to form a disulfide bridge between the terminal cysteine residues of the sequence, thereby simulating the structure of the v3 loop. Attention has been initially on a key region at the tip of the loop, which contains the sequence Gly-Leu-Gly-Gln, in contrast to the subunit Gly-Pro-Gly-Arg, which is conserved in many other viral strains.

The protein has been studied as its 1 mM solution in water by use of two-dimensional COSY, NOESY, ROESY, and TOCSY NMR techniques and variable temperature studies, at both 360 and 600 MHz. Analysis of nuclear Overhauser effects, proton-proton coupling constants, and circular dichroism spectra has shown that in the temperature range 5-27 °C, the protein adopts a flexible conformation in aqueous solution, whereas in aqueous trifluoroethanol solution, a more helical structure is formed as the concentration of trifluoroethanol is increased. The results suggest that the immunogenic specificity of the v3 loop may have a greater dependence on amino acid sequence than on a fixed secondary structure, so that antibody interaction could involve modification of the flexible conformation to one more suitable for binding.

7. **Aggregation Kinetics of Colloidal Particles Destabilized by Enzymes**

A.K. Gaigalas and H.H. Weetall

A method has been developed for the assay of several classes of enzymes by a light scattering technique using substrate coated colloidal particles. The polymeric substrate (protein, starch, DNA, or RNA) is introduced into a suspension of colloidal particles such as ferrofluid particles at the desired pH. The solution is then sonicated to induce adsorption of the polymeric substrate

on the surface of the particles. Finally a protease, amylase, or nucleic acid hydrolase is introduced into the suspension and dynamic light scattering (DLS) properties are monitored as a function of time. In the case of the protease and amylase systems, dynamic light scattering indicates a trend toward particle aggregation. A preliminary interpretation of this observation is that the coating of the particles is degraded rendering them unstable to aggregation since the bare particles are inherently unstable. Such behavior is similar to the aggregation of antibody coated latex particles which are induced by the addition of antigen. The opposite effect is seen when nucleic acid hydrolase is added to DNA coated particles, suggesting that the initial system consists of particle complexes held together by DNA strands which are hydrolysed leading to smaller aggregates. In either case, the detailed mechanism of the reaction is not known. This work addresses the case of particles coated with protein or starch which aggregate on introduction of protease or amylase. A better understanding of the mechanism will provide strategies for improving the sensitivity and utility of the assay technique.

8. Surface Enhanced Raman Spectroscopy of Biological Molecules

A.K. Gaigalas, S. Abramowitz, and V. Reipa (Institute of Chemical Technology at Vilnius, Lithuania)

Surface Enhanced Raman Spectroscopy (SERS) has proved to be a useful probe of molecules adsorbed at metal interfaces. This is significant to biological studies because the electrochemical system can serve as a model of the biological system at an interface. Due to the enhancement of the S/N ratio up to 10^6 for molecules adsorbed on the silver surfaces, it is possible to obtain well resolved spectra of analytes present at micromolar concentrations. SERS is also sensitive to the orientation and distance of the scattering molecule from the metal surface, as summarized in the so-called "surface selection rules." SERS of insulin were recorded in unbuffered Na_2SO_4 and KCl solutions (pH=6.6) at room temperature. Insulin is composed of two chains, held together by two disulfide bridges, both of which are electrochemically reducible. We observed spectroscopically the sequential disulfide bridge reduction on the silver electrode and the resulting conformational perturbations. SERS may provide insight concerning the role of the electrostatic effects in insulin monomer binding to the cellular membrane, as well as its possible conformational perturbations.

We also measured the potential dependent band shifts in the vibrational spectra of adsorbed model molecules-butanethiol and tyrosine. Measurements were performed in a standard electrochemical-optical cell with a silver electrode. The influence of the electric field on the normal modes was calculated using simplified normal coordinate code adapted to the PC. The measured shifts of the S-M, S-C, and C-C bands are consistent with the expected Stark shifts due to the presence of a strong double layer electric field.

9. Database of Thermodynamic Properties of Reactions Catalyzed by Oxidoreductases

R.N. Goldberg and Y.B. Tewari

The oxidoreductases comprise an important class of enzymes; they are assigned the first major group heading under the International Union of Biochemistry's classification scheme. We have compiled and evaluated equilibrium constants and enthalpy changes for the reactions catalyzed by oxidoreductases. For each reaction the following information is given: the reference for the data; the reaction studied; the name of the enzyme used and its Enzyme Commission number; the method of measurement; the conditions of measurement (temperature, pH, ionic strength, and the buffer(s) and cofactor(s) used); the data and an evaluation of it; and, sometimes, commentary on the data and on any corrections which have been applied to it. The data from 204 references have been examined and evaluated. This review represents an important milestone in data evaluation in biochemical thermodynamics.

We have measured enthalpies for the hydrolysis reactions of penicillin-G and related antibiotics (ampicillin and cephalosporin-C) which are catalyzed by β -lactamase. The apparent equilibrium constant has been determined at $T = 298.15$ K and $\text{pH} = 6.38$. Acid ionization constants have also been determined since they are needed for the analysis of the calorimetric and equilibrium data. Interest in this reaction stems from the fact that microbes manufacture penicillinase and use it to destroy penicillin-G and other antibiotics. A knowledge of the position of equilibrium and how it is influenced by factors such as temperature, pH, and ionic strength may be useful in understanding how this reaction works and in minimizing the extent of this reaction.

10. Statistical Mechanics of Biochemical Systems

J.B. Hubbard

We recently derived a transformation by which calculations of hydrodynamic friction of arbitrarily shaped Brownian particles are converted into much simpler electrostatic problems. This greatly facilitates the interpretation of liquid-phase diffusion data in terms of the size and shape of solvated biopolymers, protein aggregates, and other biological entities. In collaboration with workers at NIH and the Computer Services Division at NIST, we are developing rapid and accurate techniques for hydrodynamic friction computations which can be utilized in the dynamic light scattering efforts led by A.K. Gaigalas.

We have determined the kinetics of multivalent interactions of liposomes with surfaces and constructed a theory. The experimental fact that these particles remain immobilized until the last few surface bonds are ruptured invalidates the use of classical chemical kinetics, and so a more refined stochastic analysis was developed. Preliminary experimental results obtained by A.L. Plant indicate good agreement between theory and experiment, and additional studies are being planned.

11. Modeling of Complex Biochemical Reactions

W.T. Yap and R.N. Goldberg

Biochemical reactions are characterized by a multiplicity of species caused by the binding of protons and metal ions to the various substrates participating in the reaction. Thus, the apparent equilibrium constants that are measured are generally functions of pH, metal ion concentrations, and ionic strength. The mathematical treatment of this problem requires the solution of the set of non-linear equations that describe the complex equilibria in solution. At NIST, this has generally been done using a semi-analytic approach to the problem. This method of solution requires specific coding for each problem - a time consuming process that requires careful checking to avoid errors. An alternative approach is to use matrix manipulation and minimization methods for the solution of the equations. Krambeck has done this using the APL language. However, it is very important that the non-ideality be included in the model and that the code be written so that it can be coupled with available mathematical software for the purpose of regression of the parameters in the model and also for the production of graphical output. We have written a general FORTRAN program that has been used to solve the chemical equilibrium problem involving ATP hydrolysis. Although this program yields a correct answer, the convergence of the algorithm to produce the correct answer is dependent upon the nature of the initial parameter estimates given to the codes. This problem needs to be addressed and resolved before the computer program is sufficiently rugged for general routine use for chemical equilibrium equations.

12. The Structural and Functional Implications of the Deletion of the High-Affinity Calcium Binding Site from Subtilisin BPN', a Detergent Enzyme

D.T. Gallagher, G.L. Gilliland, and P. Bryan (CARB/Univ. of MD)

Subtilisins (SBTs) are a class of serine proteases which are used in a variety of commercially available household detergents. A version of subtilisin BPN' lacking the high affinity calcium site (site A) has been produced through genetic engineering methods, and its crystal structure determined and refined at 1.8 Å resolution. This protein and the corresponding version containing the calcium A site have been analyzed and compared. The deletion of residues 75-83 was made in the context of four site-specific replacements previously shown to stabilize subtilisin. The helix that in wild type is interrupted by the calcium binding loop, is continuous in the deletion mutant, with normal geometry. A few residues adjacent to the loop, principally those that were involved in calcium coordination, are repositioned and/or destabilized by the deletion. Unlike wild type and previous mutants, the calcium-independent version of subtilisin displays easily reversible refolding. This is among the largest internal changes to a protein to be described at atomic resolution.

Prior to initiating studies of structural features which affect the stability of SBT, the protease activity of the enzyme was reduced by replacing the active site serine with a cysteine. Studies of the mutations M50F, Y217K and N218S, which enhance the thermostability of SBT, were undertaken in this context. This framework also provided an opportunity to examine the structural contributions of the high-affinity, calcium ion-binding site to stability. This was done by removing residues 75-83, the A site calcium ion-binding loop. The resulting molecule, even with the three stabilizing single site mutations, is less stable than the wildtype enzyme. The first attempt to enhance the stability of this radically modified SBT was made by the introduction of a disulfide bridge at positions 22 and 87. This structure has also been recently determined and refined.

13. The Three-Dimensional Structure of Glutathione S-Transferase - an Important Detoxification Enzyme

G.L. Gilliland, X. Ji (CARB/Univ. of MD), and R. Armstrong (Univ. of MD)

The crystal structure of a mu class glutathione S-transferase (EC 2.5.1.18) from rat liver (isozyme 3-3) in complex with the physiological substrate glutathione (GSH) has been solved at 2.2 Å resolution by multiple isomorphous replacement methods. The glutathione S-transferases (EC 2.5.1.18) are a group of liver enzymes that catalyze the addition of the tripeptide glutathione to substrates bearing electrophilic functional groups. As such they are probably the single most important class of enzymes involved in detoxification of endogenous and xenobiotic substances. The enzyme crystallized in the monoclinic space group C2 with unit cell dimensions of $a = 88.0$ Å, $b = 69.1$ Å, $c = 81.3$ Å, and $\beta = 106.1^\circ$. Oligonucleotide-directed, site-specific mutagenesis played an important role in the solution of the structure in that the cysteine mutants C86S, C114S, and C173S were used to help locate the positions of mercuric ion sites in non-isomorphous derivatives with ethylmercuric phosphate and to align the sequence with the model derived from MIR phases. The dimer in the asymmetric unit refined to a crystallographic $R = 0.171$ for 19,298 data with $I \geq 1.5\sigma(I)$. The final model consists of 4,150 atoms, including all non-hydrogen atoms of 434 amino acid residues, two glutathione molecules and oxygen atoms of 474 water molecules. The dimeric enzyme is globular in shape with dimensions of 53 X 62 X 56 Å. Crystal contacts are primarily responsible for conformational differences between the two subunits which are related by a non-crystallographic 2-fold axis. The structure of the type 3 subunit can be divided into two domains separated by a short linker, a smaller α/β domain (domain I, residues 1-82) and a larger α domain (domain II, residues 90-217). Domain I contains four β -strands which form a central mixed β -sheet and three α -helices which are arranged in a $\beta\alpha\beta\alpha\beta\alpha$ motif. Domain II is composed of six α -helices. Domain I can be considered the glutathione binding domain, while domain II seems to be primarily responsible for xenobiotic substrate binding. The active site is located in a deep (19 Å) cavity which is composed of three relatively mobile structural elements; the long loop (residues 33-42) of domain I, the $\alpha 4/\alpha 5$ helix-turn-helix segment and the C-terminal tail. Glutathione is bound at the active site in an extended conformation, at one end of the β -sheet of domain I, with its backbone facing

the cavity and the sulfur pointing toward the subunit to which it is bound. Fifteen hydrogen-bond or salt-bridge contacts are involved in the interaction between glutathione and the enzyme; the hydrogen bond (3.2 Å) between the sulfur of glutathione and the side-chain hydroxyl group of tyrosine 6 is of special interest. This interaction appears to lower the pK_a of the sulfhydryl group.

14. Thermodynamics of Antibody-Antigen Interactions

F.P. Schwarz, R. Mariuzza (Institut Pasteur, Paris) and R. Poljak (Institut Pasteur, Paris, now at CARB)

Antibody molecules form tight noncovalent complexes with specific antigens that are stabilized by hydrophobic, hydrogen bond, van der Waals and ionic interactions, in common with other protein-protein association processes. There is considerable discussion about whether the driving force in protein association reactions arises from the withdrawal of apolar protein surface from water upon complex formation (the hydrophobic effect), from electrostatic interactions, or from hydrogen bond formation.

Titration calorimetry measurements show that the reactions between monoclonal antibody D1.3 and its F_v fragment with the specific antigen lysozyme are exothermic at 24.3 °C, yielding a negative enthalpy $\Delta H_b = -90.8 \pm 0.5 \text{ kJ mol}^{-1}$ for the antibody and $-90.5 \pm 1.8 \text{ kJ mol}^{-1}$, for the antibody F_v fragment. The association constant of the antigen- F_v reaction determined from the titration calorimetry measurements is $K_b = 2.3 \pm 1.0 \times 10^8 \text{ L mol}^{-1}$, yielding an entropy change of $141 \pm 7 \text{ J mol}^{-1} \text{ K}^{-1}$. Thus, this reaction is enthalpically driven, a result that correlates with the three-dimensional structure of the antigen-antibody complex.

X-ray diffraction studies of the lysozyme- F_{ab} D1.3 and of the lysozyme- F_v D1.3 complexes showed that about 15 amino acid residues of the antibody make direct contact with a similar number of residues of the antigen. These contacts include hydrogen bonds and van der Waals interactions, with no observed ion pairs. A large proportion of the contacts with the antigen are made by aromatic residues in the antibody combining site. Detailed analysis of the 1.8 Å resolution structures has revealed the presence of a significant number of water molecules in the antigen-antibody interface which fill voids not occupied by amino acid residues. In addition, most of the ordered water molecules visible in the unliganded antibody combining site are retained upon complex formation, and several additional ones are recruited to participate in an extended network bridging antigen and antibody. The recruitment upon complex formation of several additional solvent molecules from bulk water, or from a state of intermediate order, may further restrict the entropic contribution. In addition to direct protein-protein hydrogen bonds, the formation of an extensive, ordered three-dimensional network of water molecules bridging antigen and antibody gives rise to a large number of solvent-mediated hydrogen bonds which should further enhance binding. Similar results were obtained with other antibody-lysozyme antigen interactions.

15. Energetics of Lectin-Carbohydrate Interactions

F.P. Schwarz and A. Surolia (Indian Institute of Science, India)

Since lectin carbohydrate binding interactions are essentially enthalpically driven with little structural change, they can serve as model systems for relating the thermodynamics of binding to intermolecular interactions between the ligand and amino acid residues at the protein binding site.

Titration calorimetry measurements of the binding of methyl α -D-mannopyranoside (Me α Man), α -D-mannopyranoside (Man), methyl α -D-glucopyranoside (Me α Glu), and α -D-glucopyranoside (Glu) to the concanavalin A (con A), pea, and lentil lectins were performed at 281 K and 292 K in 0.01 M dimethylglutaric acid-NaOH buffer (pH 6.9) containing 0.15 M NaCl. The site binding enthalpies, ΔH , are the same at both temperatures. They range from -28.4 ± 0.9 (Me α Man) to -16.6 ± 0.5 kJ mol⁻¹ (Glu) for con A, from -26.2 ± 1.1 (Me α Man) to -12.8 ± 0.4 kJ mol⁻¹ (Me α Glu) for pea lectin, and -16.6 ± 0.7 (Me α Man) to -8.0 ± 0.2 kJ mol⁻¹ (Me α Glu) for lentil lectin. The site binding constants range from $17 \pm 1 \times 10^3$ L mol⁻¹ (Me α Man to con A at 281.2 K) to 230 ± 20 L mol⁻¹ (Glu to lentil lectin at 292.6 K) and exhibit high specificity for con A where they are in the Me α Man:Man:Me α Glu:Glu ratio of 21:4:5:1, while the corresponding ratio is 5:2:1.5:1 for pea lectin and 4:2:2:1 for lentil lectin. The higher specificity for con A indicates more interactions between the amino acid residues at the binding site and the carbohydrate ligand than for the pea and lentil lectin-carbohydrate complexes. The carbohydrate-lectin binding results exhibit enthalpy-entropy compensation in that $\Delta H_b(\text{kJ mol}^{-1}) = -16741 \pm 581 + (1.30 \pm 0.12) T(\text{K})\Delta S_b(\text{J mol}^{-1}\text{K}^{-1})$.

Differential scanning calorimetry measurements on the thermal denaturation of the lectins and their carbohydrate complexes show that the con A tetramer dissociates into monomers, while the pea and lentil lectin dimers dissociate into two sub-monomer fragments. At the denaturation temperature, one carbohydrate binds to each monomer of con A and the pea and lentil lectins. Binding of the carbohydrate increases the denaturation temperature of the lectin and the magnitude of the increases in denaturation temperature yield binding constants in agreement with the determinations from titration calorimetry.

The binding thermodynamics of 5 fluoro substituted glucopyranoside derivatives to concanavalin A have also been determined by titration calorimetry. The binding enthalpies range from 0 kJ mol⁻¹ for the substitution of the 6 and 4 carbon OH group by F to -36.7 ± 1.2 kJ mol⁻¹ for substitution of the 1 carbon OH group by F. The site binding constants at room temperature range from 137 ± 10 L mol⁻¹ for the 1-F substituted glucopyranoside to 560 ± 40 L mol⁻¹ for D-glucopyranoside. The binding thermodynamics are being compared to the energetics of the X-ray determined structures of the concanavalin A-carbohydrate complexes utilizing **CHARMm**, a software energy minimization program. This comparison is being used to correlate changes in the binding enthalpies, for example, with changes in hydrogen bond formation between the solvated structures of the ligand and lectin and the solvated complex.

16. Phospho-Protein IIA^{Glc} as a Positive Allosteric Regulator of *Escherichia coli* Adenylate Cyclase

P.T. Reddy

Genetic evidence suggests a role for Protein IIA^{Glc} of the phosphoenolpyruvate:glycose phosphotransferase system (PTS) protein(s) in the regulation of adenylate cyclase activity and consequently the level of cAMP, an important second messenger in the cell. Glucose grown cells exhibit low levels of cAMP. A working model has been derived from this observation that the state of phosphorylation of Protein IIA^{Glc} determines the concentration of cAMP. Protein IIA^{Glc} has a phosphorylatable histidine 90 and a regulatory histidine 75. In order to gain insight into the regulation of adenylate cyclase by Protein IIA^{Glc}, both the His 90 and the His 75 codons were each mutated to code for glutamine. The [Gln⁹⁰] mutation does not allow the Protein IIA^{Glc} to get phosphorylated by HPr, the second protein in the PTS phosphorylation cascade, whereas the [Gln⁷⁵] mutation allows the protein to get phosphorylated at His 90 by HPr but traps the protein in the phosphorylated state. Adenylate cyclase assays were performed in a *crr* (the gene that codes for protein IIA^{Glc}) deletion strain of *E. coli* transformed with a plasmid carrying the wild type *crr* gene as well as the mutant forms. Wild type Protein IIA^{Glc} in the phosphorylated state and [Gln⁷⁵] IIA^{Glc} are equally potent activators of adenylate cyclase. The [Gln⁹⁰] IIA^{Glc} mutant failed to activate adenylate cyclase. Taken together, these results suggest that phospho-protein IIA^{Glc} is an activator of adenylate cyclase, while the dephosphorylated form deactivates the enzyme resulting in low cAMP level in the cell.

17. Ab Initio Interaction Potentials for Molecular Systems Containing Multivalent Metal Ions

W.J. Stevens, M. Krauss, and N. Gresh (Institut de Biologie Physico-Chimique, France)

A detailed investigation of the potential energy hypersurface of Zn²⁺ binding to model oxygen-containing ligands (water, formaldehyde, formate) has been performed by large-basis set quantum-chemical computations. The decomposition of the intermolecular interaction energy into its components (Coulomb, exchange, polarization and charge-transfer) was done within the frozen fragment reduced variational space (RVS) procedure developed by Stevens and Fink (Stevens, W., and Fink, W., Chem. Phys. Letts. 139, 15, 1987). This is the first time the RVS procedure has been applied systematically for the study of cation-ligand interactions. Its use was dictated by the very large magnitudes of the second-order terms in the divalent cation complexes, and the need to separately obtain polarization and charge-transfer contributions defined within E2 in a variational sense. Concomitantly, further elaborations on the molecular mechanics procedure SIBFA were carried out. The main features of the latter involve the computation of the electrostatic and polarization energies by means of distributed multipoles and anisotropic polarizabilities derived from the large-basis set MO's of the individual fragments, the short-range

repulsion by means of an S^{*2}/R formula, and an explicit formulation of the charge-transfer energy. A very satisfactory match of the radial and angular behaviors of the corresponding *ab initio* energy contributions has been achieved.

Computations performed subsequently on di- and oligoliganded complexes of Zn^{2+} show that the SIBFA E_{pol} and E_{ct} functionals closely account for the nonadditive behaviors of the corresponding second-order energy contributions determined from the *ab initio* SCF calculations on these complexes, and their non-linear increases as a function of the number of ligands. The total intermolecular interaction energies computed with this procedure reproduce with a very good accuracy the corresponding SCF ones: this can thus be achieved without the need for additional, extraneous terms in the intermolecular potential as invariably implemented in all other molecular mechanics representation which attempt to improve on the representations of polyliganded complexes of divalent cations.

18. Cation-Aromatic Hydrogen Bonding

W.J. Stevens and H. Basch (Bar Ilan Univ., Israel)

The classical H-bond structure typically involves an oxygen, nitrogen or sulfur atom as the donor/acceptor. A more unusual type of (presumably) H-bond interaction is one between a cationic ammonium group (donor) and an aromatic system (acceptor). Many protein structures exhibit such bonding between amino acid side chains. Recent experimental results and theoretical calculations indicate that the electrostatic interaction between such groups leads to substantial binding energies (40-80 kJ/mol) in the gas phase. Binding energies of this magnitude, when accompanied by strong geometric preferences, can be important determinants for protein structural preferences. To explore the binding energetics and geometric preferences of this type of hydrogen bond, prototypical cationic amines interacting with benzene and benzene derivatives have been studied using *ab initio* quantum chemistry methods. A large number of ammonium cation-aromatic ring complexes have been geometry optimized at the 3-21G level of basis set. The optimum geometries were used in single-point 6-31G* calculations at both the Hartree-Fock and correlated (MP2) levels. The calculations reveal binding energies as high as 108 kcal/mol (ammonium + tryptophan) but weak geometric preferences associated with the exact position of the proton above the aromatic ring and the tilt of the donor group relative to the plane of the aromatic ring.

19. Elucidating the Molecular Function and Mechanism of Stress Protein Action in Replicating DNA

K.H. McKenney and J. Hoskins (CARB/Univ. of MD)

Heat-Shock proteins are normal constituents of cells whose synthesis is increased on exposure to various forms of stress. They are interesting because of their ubiquity and high conservation during evolution. Two families of heat-shock proteins, hsp60s and hsp70s have been implicated in catalyzing protein folding and assembly and also in maintaining proteins in an unfolded state, thus facilitating membrane transport. The *Escherichia coli* hsp70 analog, DnaK and two other heat shock proteins, DnaJ and GrpE are required for cell viability at high temperatures and are involved in DNA replication of phage lambda and plasmids P1 and F. We discovered and demonstrated the mechanism by which DnaK and DnaJ activate the plasmid P1 initiator, RepA for binding the P1 origin of DNA replication. Activation is the conversion of RepA dimers into monomers in an ATP dependent reaction and the monomer form binds with high affinity to origin DNA. Based on this data and previous work, we have developed a model for heat shock protein action under normal and stress conditions.

20. Engineering Molecular Tools and Genetic Techniques to Define Specific Chemical Contacts Essential for Receptor Protein Signal Recognition and Signal Transduction

K.H. McKenney and J.L. Moore

Protein-ligand interactions are responsible for regulating many biological processes essential for growth, viability and signal transduction. Protein binding of ligands frequently produces a conformational change in the protein which can significantly alter the protein's function and activity. The cyclic AMP receptor protein (CRP) of *E. coli* and its small molecule ligand, cAMP provide an important model system for studying protein-ligand interaction required for regulation of gene expression in a large number of living systems. A model of the three dimensional structure of CRP with bound cAMP, determined by x-ray crystallographic methods, was used in conjunction with molecular genetic, biochemical and biophysical methods and techniques, specific chemical side chain substitutions in CRP via codon changes in the gene coding for CRP. The purpose of this work was to define the role and function of specific chemical contacts essential for CRP function. We have discovered six pairs of amino acid side chains important for protein-ligand function in the CRP dimer. Four pairs of amino acids function as "anchor" contacts, important for recognition of the sugar and cyclic phosphate moieties on cAMP, while the other two amino acid pairs function as "specificity" contacts to recognize the purine ring of cAMP. This information, combined with previous work, has been used to develop a model for ligand induced conformation change that results in signal transduction and gene activation.

21. DNA Intercalation Fluorescence for Detection of Insecticides and Carcinogens

J.J. Horvath and A. Gupta (Indian Institute of Immunology)

The detection of carcinogens in air is a time consuming process whereby air is pushed through a urethane filter for 12-24 hours, extracted and then detected using GC or GC-MS. This process is expensive particularly since many negative samples are processed along with the positive samples. What is needed is a simple, rapid, and sensitive general assay methodology for carcinogens, which can eliminate the negative samples before further processing.

Double stranded DNA will intercalate many fluorescent dyes. Since there are a large number of intercalating areas in a typical DNA molecule, it is possible to obtain a very large signal for a small quantity of DNA. It is also well known that many carcinogenic molecules are DNA intercalating agents. Since both the dye and the carcinogen intercalate into DNA it is possible to set up a competitive binding reaction, similar to an antigen/antibody reaction, whereby the amount of intercalating dye bound is inversely proportional to the amount of carcinogen bound.

We are examining two methods of detecting the DNA competitive binding reaction. The first method involves fluorescent polarization spectroscopy. A fluorescent dye molecule, when free in solution, will exhibit little fluorescence polarization since the molecule rotates freely and quickly. A DNA intercalated dye molecule will show strong polarization because its movement is limited by the binding, and the DNA, being large, will rotate very slowly in comparison to the free dye. The second method of detection uses evanescent wave technology. Double stranded DNA is bound to the sides of an optical wave guide. The intercalation reaction is monitored in real-time by application of the evanescent wave. This method should yield a very sensitive, rapid, and potentially portable technique for detection of carcinogens.

22. Simultaneous Fluoroimmunoassay for Two or More Analytes Using Two Different Fluorophores

S.A. Glazier and M.F. McCurley

There are many different techniques for the detection and quantitation of antigen/antibody reactions. These methods include enzyme immunoassay, radio immunoassay and fluorescence immunoassay. In all these cases the systems are designed to detect only the presence of a single antigen using a specific antibody and label. In addition, all presently available immunoassay methods which quantitate high molecular weight antigens use some form of solid-phase technology.

There have been recent reports of the fabrication of fiber optic based immunosensors utilizing immobilized antibody (IgG) $F_{(ab)2}$ fragments which are labelled with dansyl chloride. Binding of antigens to these fragments leads to increases in fluorescent intensity of the labels. This

sensor employs two different isomers of dansyl chloride. The fluorescent isomers have distinct excitation and emission spectra, making it possible to follow their individual fluorescent intensities. Anti-Guinea Pig IgG, and anti-Rabbit IgG were treated to produce the $F_{(ab')_2}$ fragments. The fragments were purified and labeled with the dansyl chloride dyes. The labeled fragments were further purified to remove unreacted dye. The final products were examined for extinction and emission fluorescent spectra. The labeled dyes will next be tested after complexation with their specific antigens.

23. Detection of Individual Bacteria by Means of Microscopic and Fluorometric Techniques

S.A. Glazier

In any enclosed ecosystem or in any system where water is recycled for drinking purposes, it is imperative that the water be pure and free of any bacteria. This requirement is even more important when the source of the drinking water is initially loaded with coliforms and other potentially harmful organisms. The ability to detect an individual bacterium and to determine whether the observed bacterium is living or dead becomes extremely important.

This project is to devise methods for the detection of an individual bacterium and to determine the viability of the organism. Detection methods under study include the application of bacterial native fluorescence as a means for detection. By use of proper filters, lighting, and photon counting it is possible to detect the presence of an individual organism under the lens of a fluorescent microscope. Studies are underway to determine whether the fluorescent signature of a viable organism is sufficiently distinct from that of a non-viable organism. If the method proves feasible, plans call for development of a breadboard model of a detection system for monitoring drinking water.

In order to examine the differences in fluorescence between viable and nonviable bacteria, numerous fluorescence spectra from *E. coli* were acquired. The bacteria were both living and killed by such reagents as UV radiation, acid, and sodium azide. At the present time however, little difference in the spectra of viable and nonviable bacteria can be seen.

Progress is now being made on determining bacteria presence by native fluorescence on the surface of a silver metal membrane filter. Ideally, one could pass a volume of water through such a filter and collect all of the bacteria in the water sample and scan the filter using fluorescence to determine the presence of bacteria. The present work is directed at confirming that an individual bacterium is detectable on the surface of a silver filter.

24. Quantitation of an Analyte by Enzymatically Mediated Fluorescence Quenching and Enhancement within Hydrogels Using Fiber Optic Methods

M.F. McCurley

Studies are underway to examine the application of a new type of biosensor based on polymer swelling coupled with fluorescence quenching. The sensing element is a crosslinked polymer which changes size or pH as a function of analyte concentration.

A pH sensitive fluorescent dye has been covalently attached to the hydrogel along with an enzyme specific for the analyte of interest. The enzyme acts on the analyte producing either acid or base. The change in pH can be monitored by the quenching/enhancement of fluorescence of the coupled dye. In the case of the pH insensitive dye the quenching is caused by the shrinking of the gel which decreases the concentration of the fluorophore resulting in concentration quenching.

Fiber optic biosensors based on these techniques offer several potential advantages over some of the commercially available devices. They can be designed so that the optical measurement, which is separated from the polymer by a diaphragm can not be affected by the optical properties of the sample. Measurements can be made in the near infrared region of the spectrum and take advantage of inexpensive components available for fiber optic communications.

A sensor has been prepared which uses glucose oxidase attached to an amide-containing acrylate polymer hydrogel. A fluorescent dye has also been incorporated in to the gel. The enzyme catalyzes the oxidation of glucose to gluconic acid, which protonates the amine. This chemical reaction either changes the pH of the gel environment or causes the gel to shrink, depending on the degree of gel crosslinking.

This work demonstrates a new, generic approach to optical sensing. It is anticipated that it will lead to a family of sensors that are both inexpensive and rugged with applications in areas where the ruggedness is important, as in environmental monitoring.

25. Determination of the Mechanism of Action of Strep α -toxin Ion Channels in LB Films

J.J. Kasianowicz

The organism streptomyces produces a toxin which is capable of forming pores in the membrane of host cells. These pores consist of a group of toxin molecules situated in a circular pattern with a center pore. This pore actually makes contact with both the inside and outside of the cell membrane, allowing the flow of ions through the pore (across the membrane). It has been

demonstrated that by applying an electric potential across the pore produced by the α -toxin it can be opened and closed. The mechanism of this opening and closing is not understood.

This work will elucidate the mechanism responsible for the opening and closing of the α -toxin pore. Mutant toxin molecules have been prepared with substitutions made in those amino acids thought to be responsible for the opening and closing function. These mutant toxins will be examined by embedding them in Langmuir-Blodgett films. The toxins will then be characterized using electrical means to compare the mutant toxins to the native α -toxin molecules. Observed differences should lead to determination of the mechanism of action.

26. Immobilization and Kinetic Characterization of Bacteriorhodopsin Entrapped in Organic Matrices and Sol-Gel Glasses

H.H. Weetall, B. Robertson, and D. Cullin (Naval Surface Weapons Testing Laboratory, Dalgren, VA)

Bacteriorhodopsin (BR) is a light sensitive membrane bound protein found in a species of bacteria which uses these proteins for homeostasis. The proteins, when exposed to visible light at 575 nm pumps protons from one side of the cell membrane to the other side. In this process the molecule shows distinct changes in its spectroscopic characteristics. The mechanism of action of bacteriorhodopsin is still not well understood. Although it is one of the most studied light-sensitive proteins, many of its physical characteristics still cannot be explained, based on the present models of the proteins proton pumping cycle.

We plan to use the ability of the molecule to be modified by passage of an electrical current as a means of studying its characteristics. The proteins spectral characteristics can be modified by passage of an electrical current across the molecule. In addition the change in the spectra caused by photon activation causes an electric current to flow based on the proton pumping across the membrane. We plan to prepare lipid membranes containing BR and excite the molecules both electrical and visibly, following the changes which occur. It is expected that these changes will be related to the actual mechanism of the proteins proton pumping action. In addition to better understanding the characteristics of this molecule we are preparing stable gelatin films and sol-gel glass adducts of this protein.

The films are being examined for stability, resolution, and reversibility and for use as materials for the storage and recovery of information (data) by changing the optical properties of the protein upon exposure to light.

The sol-gel glass entrapped BR shows retention of biological activity. However, as the glass dries the cycling process appears to increase in speed. The cause of this phenomenon is under investigation.

27. Examination of Cooperative Interactions Between Proteins and Lipids in Lipid Membranes

A.L. Plant

Lipid and protein molecules embedded in phospholipid bilayer membranes are capable of two dimensional movement in the plane of the bilayer. For a multivalent receptor-ligand pair, this movement allows the formation of multiple bonds per molecule at the membrane surface. This kind of interaction can result in aggregation of reactants in patches in the membrane. Because multiple bonds can be formed simultaneously, multivalency strongly affects the binding constants and the dissociation times. Using antigens/antibodies we have modeled the effect of multivalency on dissociation kinetics and binding constants.

Studies are now underway to devise methods for studying the effects of multivalent interactions on planar membrane microstructure. The preparation of planar lipid membranes starts with the formation of a lipophilic monolayer by applying alkylthiols to gold surfaces. Lipids, proteins and other molecules present in the membranes of liposomes should be transferrable to this monolayer, forming a bilayer containing the molecules of interest. We have successfully formed phospholipid containing bilayers on gold and are studying their physical and electrochemical properties. By varying the molecules embedded into the second layer of the bilayer a variety of studies are possible related to cooperativity, ion transport across the bilayer and electrochemical effects of the bound materials. Thus far, we have shown by changes in electrochemical characteristics that the small protein, melittin, the active ingredient of bee venom, interacts with these membranes in a manner consistent with its interaction with natural cell membranes. These results suggest that melittin monomers aggregate within the bilayer to form pores through which charged species can now pass through the otherwise impermeable lipid membrane. These studies should help elucidate the characteristics of the bilayer, the two dimensional movement of the embedded molecules and the cooperativity issue.

**C. Outputs and Interactions
(Biotechnology Division)**

1. Publications

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2. Talks

- Abramowitz, S. and Yap, W.T., "Thermodynamic Data of Use to Bioprocess Engineering," 9th International Biotechnology Symposium, Crystal City, VA, August 21, 1992.
- Astumian, R.D., "Electroconformational Coupling and Free Energy Transduction," Universitat Bielefeld, Germany, November 20, 1991.
- Astumian, R.D., "Conductivity and Optical Properties of DNA in an Electric Field," Universitat Bielefeld, Germany, November 20, 1991.
- Astumian, R.D., "Using Electric Fields to Probe Membrane Reactions," NIH, December 13, 1991.
- Astumian, R.D., "Frequency Dependence of Transport Across Membranes in an AC Field," University of Montreal, February 14, 1992.
- Astumian, R.D., "Relaxation Kinetics of Membrane Enzymes" (Poster Session), Zurich, Switzerland, January 22, 1992.
- Astumian, R.D., "Membrane Protein Damage in Electrical Injury," Orlando, FL, October 31, 1991.
- Cole, K.D., "Two-Dimensional Gel Electrophoresis of Soybean Proteins Used to Compare Protein Separations in Crude Mixtures," Electrophoresis Society Meeting, Raleigh-Durham, NC, June 23, 1992.
- Cole, K.D., "Application of Salt-Polymer Aqueous Two-Phase Extraction Systems to Purify Proteins and Nucleic Acids From Complex Mixtures," Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, PA, September 23, 1992.
- Coxon, B., "NMR Studies of Cyclobutanetetraone Phenylhydrazone, and Anilides," Washington Area NMR Group Minisymposium, NIH, October 18, 1991.
- Dizdaroglu, M.M., "Free Radical-Induced DNA Damage in Chromatin *in vitro* and *in vivo*," Oxygen Club of the Greater Washington Area, National Naval Medical Center, Bethesda, MD, October 8, 1991. Invited
- Dizdaroglu, M.M., "Measurement of Oxidative DNA Damage in Mammalian Chromatin by GC/MS," Hewlett-Packard Users' Meeting, Washington, DC, May 31, 1992. Invited

- Dizdaroglu, M.M., "DNA Base Damage and DNA-Protein Cross-links in Chromatin of γ -Irradiated or H_2O_2 -Treated Cultured Human Cells," VI Biennial Meeting of the International Society of Free Radical Research, Turin, Italy, June 20, 1992. Invited
- Dizdaroglu, M.M., "Free Radical-Induced DNA Damage in Mammalian Cells," Department of Clinical Biochemistry, Medical School, Bydgoszcz, Poland, June 22, 1992. Invited
- Dizdaroglu, M.M., "Chemical Determination of Free Radical-Induced Damage to DNA," Institute of Human Genetics of the Polish Academy of Sciences, Poznan, Poland, June 24, 1992. Invited
- Dizdaroglu, M.M., "DNA Damage by Free Radicals," Faculty of Pharmacy, University of Ankara, Ankara, Turkey, July 24, 1992. Invited
- Dizdaroglu, M.M., "Mechanisms of Free Radical DNA Damage in Mammalian Chromatin," NIST, Organic Analytical Research Division, August 19, 1992. Invited
- Edwards, J.J., "Characterization of Soybeans Using Two-dimensional Gel Electrophoresis and Size Exclusion Chromatography: Analysis of Protease Inhibitors, Storage Proteins and Isoflavones," ACS International Meeting on Biotechnology, Crystal City, VA, August 19, 1992.
- Gawrisch, K., and Coxon, B. (Poster Co-presenters), Ferretti, J.A., Blomber, J., and Pipkorn, R., "The 3D Structure of a Cyclic Peptide Which Represents the V3 Neutralization Loop of GP120," Abstract for NIH Research Festival 1992, NIH, Bethesda, MD, September 22, 1992.
- Gilliland, G.L., "The Biological Macromolecule Crystallization Database: An Update," The Annual American Crystallographic Association Meeting and Pittsburgh Diffraction Conference, Pittsburgh, PA, August 1992. Invited
- Gilliland, G.L., "Crystal Structure Analysis of Subtilisin BPN' Mutants Engineered for Studying Thermal Stability," Chalmers University and University of Goteborg, Goteborg, Sweden, September 1992. Invited
- Gilliland, G.L., "Crystal Structure Analysis of Subtilisin BPN' Mutants Engineered for Studying Thermal Stability," International Symposium on Subtilisin Enzymes, Hamburg, Germany, September 1992. Invited
- Glazier, S. and McCurley, M., "Dual Analyte Fiber Optic Immunosensors Employing Antibody Fragments Labelled with Environmental Sensitive Dyes," 204th ACS National Meeting, Washington, DC, 1992.

- Glazier, S. and Horvath, J., "Fluorescence Measurement of Tetracycline in Bacterial Fermentations," 9th International Biotechnology Symposium, Crystal City, VA, 1992.
- Glazier, S., "The Utilization of Nonlinear Optical Properties of Organometallic Compounds for Anion Detection," 204th ACS National Meeting, Washington, DC, 1992.
- Goldberg, R.N., "Thermochemistry of the Hydrolysis of L-arginine to (L-citrulline + ammonia) and of the Hydrolysis of L-arginine to (L-ornithine + Urea)," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, August 18, 1992.
- Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions: Oxidoreductases," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, August 18, 1992.
- Goldberg, R.N., "Thermodynamic Data of Use to Bioprocess Engineering," 9th International Biotechnology Symposium, Crystal City, VA August 20, 1992.
- Grabbe, E.S., "Use of Total Internal Reflection Fluorescence with Energy Transfer for Characterizing Adsorbed Protein Layers on Thin Nylon Films: A Method for Biosensor Analysis," 18th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) and the 13th Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA, October 8, 1991.
- Gray, M., Williams, J., Plant, A.L., MacCrehan, W., and May, W., "Automated Immunoassays for Measurement of Lipoprotein Cholesterol," AOAC International Meeting, Cincinnati, OH, September 1992.
- Hancock, D.K., "Structure Determination of an Unique Pyoverdine-Type Siderophore from *Pseudomonas fluorescens* 244," 33rd ENC, Asilomar, CA, April 1, 1992.
- Kline, M.C., "Human Identification Using Amplified Fragment Length Polymorphisms from Hair Roots and a Moving Boundary Electrophoresis System," Electrophoresis Society Meeting, Raleigh-Durham, NC, June 22, 1992.
- Krauss, M., "Model of the Active Site Spectroscopy of the Rhodanese Enzyme," Scientific Conference on Chemical Defense Research-U.S. Army, Aberdeen Proving Ground, MD, November 1991.
- Krauss, M., "Active Site Analogues and the Mechanism of Carbonic Anhydrase," Sanibel Scientific Conference on Theoretical Biochemistry, St. Augustine, FL, March 1992.
Invited
- Krauss, M., "Assignment of Radical Spectra in Oxidized Cytochrome c Peroxidase," Mt. Sinai Medical Center, Biophysics Department, New York, June 1992.

- Krauss, M., "Assignment of Anion and Radical Spectra in Proteins," Canadian Theoretical Chemistry Conference, Montreal, Canada, August 1992.
- Major, P. and Plant, A.L., "Liposome Immunosorbant Assay (LISA) for Determination of Staphylococcal Enterotoxin B," 3rd World Congress on Foodborne Infections and Intoxications, Berlin, June, 1992.
- McCurley, M.F., "Optical Sensor Based on Polymer Swelling Coupled to a Change in Fluorescence," 19th FACSS Meeting, Philadelphia, PA, 1992.
- McKenney, K.H., "Tools of Molecular Engineering," The George Washington University School of Medicine, Department of Biochemistry and Molecular Biology, Washington, DC, February 1992.
- McKenney, K.H., "Elucidating Protein Function and Structure," The George Washington University School of Medicine, Department of Biochemistry and Molecular Biology, Washington, DC, February 1992.
- McKenney, K.H., "Role of Heat Shock Proteins in DNA Replication," The George Washington University, Department of Genetics, March 1992.
- McKenney, K.H., "Function of DnaK and DnaJ in the Activation of the RepA Replication Initiator Protein," FASEB Meeting on Protein Folding, Saxtons River, VT, June 1992.
- McKenney, K.H., "Molecular Biology at CARB," Maryland State Governor's Academy for Mathematics, Science and Technology, NIST, July 1992.
- Plant, A.L. and Tarlov, M., "In Search of a Convenient and Stable Substrate for Planar Model Membranes: Investigations, on the Use of Alkane Thiols in Preparing Lipid Membrane Electrodes," Copper Mountain, CO, June 14, 1992.
- Reddy, P., "The Phosphorylated Form of IIA^{Glc} of the Phosphoenolpyruvate-sugar Phosphotransferase System is a Positive Allosteric Modulator of Adenylate Cyclase of *E. coli*," American Society of Biochemistry and Molecular Biology, Houston, TX, February 1992.
- Reddy, P., "Cloning and Expression of Lethal Gene Products in *E. coli*: Adenylate Cyclase as a Model System," University of Delhi, South Campus, July 1992.
- Reddy, P., "Regulation of *E. coli* Adenylate Cyclase Activity by the Phosphorylated Form of IIA^{Glc} of the Phosphoenolpyruvate-sugar Phosphotransferase System," University of Delhi, South Campus, July 1992.

- Reddy, P., "Dissection of the Catalytic and Regulatory Domains of *E. coli* Adenylate Cyclase," Delhi University College of Medical Sciences, August 1992.
- Reddy, P., "Cloning and Expression of the Phosphoenolpyruvate-sugar Phosphotransferase System Proteins of *E. coli*," Center for Biochemicals, Council for Scientific and Industrial Research, Delhi, August 1992.
- Reddy, P., "Expression of Lethal Gene Products in *E. coli*," Department of Biochemistry, Indian Agricultural Research Institute, New Delhi, August 1992.
- Reeder, D.J., "NIST Program in Biosensor Research," NASA/JPL Meeting on Sensor Needs, Pasadena, CA. November 6, 1991.
- Reeder, D.J., "Use of Capillary Electrophoresis in DNA PCR Analysis," Southwest Institute of Forensic Sciences, Dallas, TX, November 21, 1991. Invited
- Reeder, D.J., "DNA Analytical Methods on Standards Development for DNA RFLP Measurements," Texas Technical Working Group for DNA Analytical Methods, Austin, TX, November 23, 1991. Invited
- Reeder, D.J., "Analysis of Prototype SRM for DNA Profiling," Technical Working Group on DNA Analysis Methods (TWGDAM) Meeting, Quantico, VA, December, 9, 1991. Invited
- Reeder, D.J., "NIST Accomplishments on DNA Research," 44th Annual Meeting of the American Academy of Forensic Sciences, New Orleans, LA, February, 17, 1992. Invited
- Reeder, D.J., "NIST DNA Standards Reference Material," 44th Annual Meeting of the Forensic Sciences, New Orleans, LA, February 21, 1992. Invited
- Reeder, D.J., "DNA Profiling," Lehigh University, Bethlehem, PA, March 26, 1992. Invited
- Reeder, D.J., "Methods and NIST Standards for DNA Profiling," Northern Illinois University, Dekalb, IL, March 27, 1992.
- Reeder, D.J., "Certification of NIST Standard for DNA RFLP Quality Assurance," Third International Symposium on Human Identification, Scottsdale, AZ, April 30, 1992. Invited
- Reeder, D.J., "NIST Standards Update and Report on SRM for RFLP Analysis," Technical Working Group on DNA Analysis Methods (TWGDAM) Meeting, Quantico, VA, June 29, 1992. Invited

- Reeder, D.J., "High-Resolution Methods for DNA Polymerase Chain Reaction Products," XIX Federation of Analytical Chemistry and Spectroscopy Societies Conference, Philadelphia, PA, September 23, 1992.
- Reipa, V., "Surface Enhanced Raman Spectra of Bovine Insulin," Indianapolis, IN, March 17, 1992.
- Reipa, V., "Influence of the Electric Field on the Tyrosine Vibrational Modes," Washington, DC, August 23, 1992.
- Robertson, B., "Nonequilibrium Thermodynamics," University of Wyoming, Laramie, WY, May 15, 1992.
- Robertson, B., "Statistical Mechanical Derivation of Nonequilibrium Thermodynamics, Symposium on Physics and Probability," University of Wyoming, Laramie, WY, 1992.
- Sachs, J.R., "Lungs, Knees, and Gels: Mathematical Models in Physiology and Biotechnology," NIH, DCRT Seminar Series, March 6, 1992.
- Sachs, J.R., "A Fast Method for the Solution of Mixed Boundary Value Problems, and an Application to Electromechanical Spectroscopy," Daniel H. Wagner Associates, Paoli, PA, March 9, 1992.
- Sachs, J.R., "Continuum Electromechanics and Numerical Analysis," Daniel H. Wagner Associates, Paoli, PA, February 21, 1992.
- Sachs, J.R., "Electromechanical Spectroscopy and a Boundary Collocation Method for Separable PDE's with Mixed BC's," University of Colorado, Mathematics Department, Denver, CO, October 15, 1991.
- Sachs, J.R., "A Fast Method for the Solution of Mixed Boundary Value Problems, and an Application to Electromechanical Spectroscopy," Kodak Research Laboratories, Rochester, NY, April 27, 1991.
- Sachs, J.R., "A Fast Method for the Solution of Mixed Boundary Value Problems," and an Application to Electromechanical Spectroscopy, Wolfram Research Institute, Champaign, IL, March 26, 1992.
- Schwarz, F.P., "Thermodynamics of Lectin-Ligand Interactions," Molecular Biophysics Unit, Indian Institute of Science, Bangalore, India, October 1991. Invited

Schwarz, F.P., "Thermodynamics of Lectin-Metal Ion and Lectin-Carbohydrate Interactions," Chemistry Department, Indian Institute of Technology, Bombay, India, October 1991.
Invited

Schwarz, F.P., "Thermodynamics of Monosaccharide Binding to Concanavalin A, Pea (*Pisum sativum*) Lectin and Lentil (*Lens culinaris*) Lectin," 12th IUPAC Conference on Chemical Thermodynamics & The 47th Calorimetry Conference, Snowbird, Utah, August 1992.

Tarlov, M. and Plant, A.L., "Ultrathin Amperometric Enzyme Electrodes Based on Biotin-Avidin Coupling at Self-Assembled Alkanethiol Monolayers on Gold," AIChE: Materials Utilized in Biosensors, Miami, FL, 1992.

Tewari, Y.B., "Application of Thermodynamics to Biotechnology," International Enzyme Biotechnology Symposium, Veracruz, Mexico, October 24, 1991.

Weetall, H.H., A Series of 12 Lectures at Universities and Institutes in India during the month of January 1992. Talks were on the following topics: Enzyme Immobilization, Biosensors, Immunoassay Methodology.

Weetall, H.H., "Biosensor Technology, A Presentation to the Clinical Division," DA, Rockville, MD, March 3, 1992.

Weetall, H.H., "Dynamic Light-Scattering for the Characterization of Reactions Between Antigen Coated Colloidal Particles and Specific Antibodies," Anchorage, AK, July 22, 1992.

Weetall, H.H., "Enzyme Assay Using Dynamic Light-Scattering of Substrate Coated Colloidal Particles," Anchorage, AK, July 23, 1992.

3. Cooperative Research and Development Agreements (CRADA) and Consortia

Consortium on Advanced Biosensors, Howard H. Weetall
Presently under development with 20-30 companies

The Integration of Crystallization Robotics and the NIST/CARB Biological Macromolecule Database to Include the Incorporation of Software for Tracking and Monitoring Crystallization Experiments, Gary L. Gilliland
ICN Biomedicals, Inc. (CRADA)

The Integration of Software and Graphics for Structural Biology on the IBM RISC System/6000 Series Workstations, Gary L. Gilliland
IBM Corporation (CRADA)

4. Patent Awards and Applications

Hancock, D.K., "Use of β -Hydroxyhistidine, 4-(1-Hydroxy-1-alkyl)Imidazole or Derivatives Thereof as Bidentate Ligands in Chelating Agents" (Submitted September 1991)

Reeder, D.J. and R.C. Allen, "Matrix Modification in the Electrophoretic Separation of Nucleic Acids" (Submitted June 1991)

Weetall, H.H., "Device and Method for Detection of Compounds Which Intercalate with Nucleic Acids" (Submitted August 1991)

Weetall, H.H. and Gaigalas, A.K., "Method and Material for the Assay of Several Classes of Enzymes by Light-Scattering Techniques Using Substrate Coated Colloidal Particles" (Submitted December 1991)

5. SRM Activities

SRM 2390 DNA Profiling Standard (certified)

SRM 927b Bovine Albumin (completed)

6. SRD Activities

NIST/CARB Biological Macromolecule Crystallization Database (Update)

7. Calibrations

None

8. Committee Assignments

S. Abramowitz

Manufacturing/Bioprocessing Working Group of the Biotechnology
Research Subcommittee of the FCCSET Committee on Life Sciences and
Health (Chairman)

Technical Review Panel, Advanced Technology Program (Chairman)

Source Evaluation Board, Advanced Technology Program

B. Coxon

Washington Area Nuclear Magnetic Resonance Group

J.J. Edwards

Biotechnology Subcommittee on Terminology, ASTM E-48.91 (Chairman)
Characterization and Identification of Biological Systems, ASTM E-48.02 (Task Group Leader)

D.K. Hancock

United States National Committee on Uniform Methods of Sugar Analysis and the International Committee on Uniform Methods of Sugar Analysis (ICUMSA), Subject 4, polarimetry and quartz plate

G.L. Gilliland

Reviewer of SBIR's on the Special Study Section 6C of the National Institutes of Health
Chairman of the NASA Biotechnology Working Group and as such, sit on the Microgravity Science and Applications Subcommittee of the Space Science and Applications Advisory Committee

NIH Molecular and Cellular Biophysics Study Section (BBCA)

NIH Special Review Committee for program project grants in response to RFA entitled Structural Biology as Applied to the Problem of Targeted Drug Design, with Potential Applicability to the Treatment of Aids

Working Group on Infrastructure, Biotechnology Research Subcommittee of the FCCSET Committee on Life Sciences and Health

Working Group on Structural Biology of the Biotechnology Research Subcommittee of the FCCSET Committee on Life Sciences and Health

NASA Biotechnology Working Group, and, as such, sit on the Microgravity Science and Applications Subcommittee of the Space Science and Applications Advisory Committee (Chairman)

CARB Board of Overseers

M. Krauss

Advanced Technology Program site visit on Density Functional Theory Project of the Biosym Corp., San Diego, CA

M.F. McCurley

Sigma Xi Education Committee

Employment Bureau, Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) Conference 1992 Committee (Chairman)

K.H. McKenney

NIST ATP site visit team, Agridyne Co., Salt Lake City, UT

NIH Human Genome study section (Member, reviewer)

American Type Culture Collection Plasmid Biology Section Review (Chairman)

PhD Examining Committee, Department of Genetics, The George Washington University, Washington, DC (three committees)

L.J. Powell

Biotechnology Research Subcommittee of the FCCSET
Committee on Life Sciences and Health (DoC Representative)
Technology Transfer Working Group (Chairman)
ACS Committee on Budget and Finance
Women Chemists Committee (Associate Member)
National Task Force on National Chemistry Week
Biochemical Technology Division Liaison to ACS Materials Secretariat
NIST Liaison to ACS
ASTM E-48 (2nd Vice Chair)
Board of Managers, Chemical Society of Washington
CARB Board of Overseers

P. Reddy

ATCC Committee to evaluate several expression vectors in the ATCC catalogue

D.J. Reeder

AACC Committee on Standards, Study Group on Total Serum Protein
ASTM E-48 on Biotechnology
Advisory Committee for the Institute of Forensic Anthropology and Human Identification
CAP Forensic Identity/Parentage DNA Proficiency Testing Task Force
Electrophoresis Society (President)
IFCC Expert Panel on Drug Effects in Clinical Chemistry (Associate Member)
NIST Animal Care and Use Committee (Chair)
NCCLS Subcommittee on Total Protein
NCCLS Area Committee on Molecular Methods
Technical Working Group on DNA Analysis Methods (TWGDAM) Quality Assurance Subcommittee

F.P. Schwarz

IUPAC exploratory sub-committee on Data Base of the Thermodynamic Stabilities of Natural and Mutant Proteins, part of the Steering Committee on Biophysical Chemistry

W.J. Stevens

CARB Board of Overseers (as Acting Director, CARB)

9. Editorships**M.M. Dizdaroglu**

Free Radical Research Communications

F.P. Schwarz

Washington Editorial Review Board
J. Phys. Chem., J. Chem & Eng. Data, and Structural Chemistry (Reviewer)

H.H. Weetall

Advances in Biotechnology (Editorial Board)
Process Biotechnology (Editorial Board)
Applied Biochemistry and Biotechnology (Executive Editor)
Trends in Biotechnology (Editorial Board)

10. Seminars

October 7, 1991

Dr. Sarah Woodson, Department of Chemistry and Biochemistry, University of Maryland, "Long-Range Folding in Self-Splicing, RNA." (Division Sponsor: G.L. Gilliland)

October 10, 1991

P.V. Sundaram, Director, Centre for Protein Engineering and Biomedical Research, Adyan, Madras, India, "Protein Cross-Linking and Stabilization." (Division Sponsor: H.H. Weetall)

October 21, 1991

Dr. Andrew Storer, Biotechnology Research Institute, National Research Council of Canada, "Protein Engineering of Cysteine Proteases: Probing Enzymatic Mechanism and Specificity." (Division Sponsor: G.L. Gilliland)

November 4, 1991

Dr. Elizabeth Howell, Department of Biochemistry, University of Tennessee, "Comparative Structure-Function Studies of *E. coli* Dihydrofolate Reductase (DHFR) and a Novel R-Plasmid Enclosed DHFR." (Division Sponsor: G.L. Gilliland)

November 5, 1991

Dr. Pamela Holbrook, Laboratory of Bioorganic Chemistry, NIDDK/NIH, "Studying Biological Signal Transduction with Mass Spectroscopy." (Division Sponsor: A.L. Plant)

December 2, 1991

Dr. Patricia Weber, Central Research and Development, Dupont-Merck Pharmaceutical Co., "Thermodynamic and Crystallographic Comparison of Natural and Synthetic Ligands Bound to Streptavidin." (Division Sponsor: G.L. Gilliland)

December 3, 1991

Dr. James Mitchell, Director, Radiation Oncology Branch, Division of Cancer Treatment, NCI/NIH, "Nitroxides and Protectors Against Oxidative Stress in Mammalian Cells." (Division Sponsor: M.M. Dizdaroglu)

December 9, 1991

Dr. Enrico Bucci, Department of Biological Chemistry, University of Maryland Medical School, "Structure-Function of Hemoglobin Explored by Time-Resolved Fluorescence Spectroscopy." (Division Sponsor: G.L. Gilliland)

December 10, 1992

Dr. Jacques Laval, Senior Staff, Institut Gustave-Roussy, "Enzymatic Repair of Lesions in DNA Generated by Alkylating Agents and Free Radicals." (Division Sponsor: M.M. Dizdaroglu)

December 16, 1991

Dr. Anthony Gatenby, Central Research and Development, Dupont Co., "The Role of Chaperones in Protein Folding: GroE Heat Shock Proteins." (Division Sponsor: G.L. Gilliland)

January 8, 1992

Dr. Heriberto Cabezas, Jr., Department of Chemical Engineering, University of Arizona, "Thermodynamic Analysis of the Aqueous Two-Phase Partitioning of Proteins." (Division Sponsor: K.D. Cole)

January 13, 1992

Dr. Graham Walker, Department of Biology, Massachusetts Institute of Technology, "Intertwining of Regulation and Function in *E. coli* Proteins Induced by DNA Damage and Stress." (Division Sponsor: G.L. Gilliland)

January 27, 1992

Dr. Arthur Pardi, Department of Chemistry, University of Colorado, "Solution Structural Studies of RNA." (Division Sponsor: G.L. Gilliland)

February 19, 1992

Ann E. Tate, Molecular Computing Program, Naval Surface Weapons Testing Laboratory, Dahlgren, Virginia, "What is Biomolecular Electronics and Computing Anyway?" (Division Sponsor: H.H. Weetall)

February 24, 1992

Dr. Mario Amsel, Department of Biophysics, Johns Hopkins School of Medicine, "Recognition of Angiotensin II: 3-Dimensional Structure of an F_{ab} - Hormone Complex." (Division Sponsor: G.L. Gilliland)

February 24, 1992

Dr. Paul W. Doetsch, Associate Professor, Emory University, School of Medicine, Atlanta, GA, "Recent Advances in Understanding the Biochemistry and Molecular Biology of Radiation-Induced DNA Damage and Repair." (Division Sponsor: M.M. Dizdaroglu)

March 2, 1992

Dr. Howard K. Schachman, Department of Molecular and Cell Biology, University of California, Berkeley, "Formation of Active Enzyme From Defective and Incomplete Polypeptide Chains: ATCase has not yet retired." (Division Sponsor: G.L. Gilliland)

March 13, 1992

Dr. Ronald A. Siegel, School of Pharmacy, University of California, "Swelling Equilibria and Kinetics in Hydrophobic Polyelectrolyte Gels with Applications to Drugs." (Division Sponsor: J.R. Sachs)

March 16, 1992

David Zopf, M.D., "Weak Affinity Chromatography: An Emerging Method for Analysis and Isolation of Oligo." (Division Sponsor: A.L. Plant)

March 16, 1992

Dr. David Draper, Department of Chemistry, Johns Hopkins University, "RNA Tertiary Structures and Conformational Switches." (Division Sponsor: G.L. Gilliland)

April 6, 1992

Dr. C. Nick Pace, Department of Medical Biochemistry and Genetics, Texas A&M College of Medicine, "Contributions of Hydrogen Bonding and the Hydrophobic Effect to the Conformational Stability of Ribonuclease T1." (Division Sponsor: G.L. Gilliland)

April 9, 1992

Professor Avadhesdi Surolia, Molecular Biophysics Unit, Indian Institute of Science, Bangalore, India, "Thermodynamic Analysis of Ligand Binding to the Winged Bean Acidic Agglutinin." (Division Sponsor: F.P. Schwarz)

April 27, 1992

Dr. Rodney Biltonen, Department of Pharmacology, University of Virginia, "Thermodynamics of Structural Transitions in Bilayer Membranes." (Division Sponsor: G.L. Gilliland)

May 11, 1992

Dr. Anna El'skaya, Head, Department of Translation and Ukrainian Biosensor Center, Institute of Molecular Biology, "Enzyme and Immunochemical Biosensors Based on Microelectronics Technology." (Division Sponsor: A.L. Plant)

May 11, 1992

Dr. Debra Dunaway-Mariano, Department of Chemistry and Biochemistry, University of Maryland, "Domain Movement Linking Catalytic Sites in the Enzyme Pyruvate Phosphate Di-kinase." (Division Sponsor: G.L. Gilliland)

May 28, 1992

Dr. Steve Goodman, Laboratory of Molecular Biology, NIH, "Role of *E. coli* Integration Host Factor in Lambda Site Specific Recombination." (Division Sponsor: R.D. Astumian)

June 5, 1992

Prof. M.R.N. Murthy, Indian Institute of Science, Bangalore, India, "Structure and Sequence of Sesbania Mosaic Virus." (Division Sponsor: G.L. Gilliland)

June 11, 1992

Dr. J.C. Ahluwala, Indian Institute of Technology, "Thermodynamic Aspects of Stability in Proteins." (Division Sponsor: R.N. Goldberg)

July 7, 1992

Dr. Martin Bier, Department of Biology, Free University, Berlin, Germany, "Cell-cell Signalling." (Division Sponsor: R.D. Astumian)

July 8, 1992

Dr. Norm Sheppard, Department of Biomedical Engineering, The Johns Hopkins University, Baltimore, Maryland, "Microfabricated Conductimetric Sensors Based on pH-Sensitive Hydrogels." (Division Sponsor: M.F. McCurley)

August 14, 1992

Gilbert Olson, Chemical Research Development and Engineering Center, Aberdeen Proving Ground, Aberdeen, Maryland, "The XM294 T2 Toxin Detector." (Division Sponsor: S. Abramowitz)

August 21, 1992

Dr. Andrzej Sokalski, Wroclaw Technical University, Wroclaw, Poland, "Protein Fields and Reactivity." (Division Sponsor: M. Krauss)

September 17, 1992

Professor K.R.K. Easwaran, Chairman, Molecular Biophysics Unit, Indian Institute of Science, Bangalore, India, "Structure and Aggregation of Calcium Ionophore, A23187, and Its Interaction with Model Membranes." (Division Sponsor: F.P. Schwarz)

September 29, 1992

Prof. Marco Colombini, Professor, Department of Zoology, University of Maryland,
"Voltage Gating in the Mitochondrial Channel, VDAC." (Division Sponsor:
H.H. Weetall)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

May 6-8, 1992

Co-chaired Mid-Atlantic Protein Crystallography Workshop, CARB, Rockville, MD
(G.L. Gilliland)

August 18-21, 1992

NSF Seminar on Microfabrication and Biosensors (H.H. Weetall)

II. Chemical Engineering Division (832)

Blaine Bateman, Chief

A. Division Overview

The Chemical Engineering program emphasized a renewed focus on long range planning in FY92. Our goals were to rebuild after the consolidation and program transfers of recent years, and establish a clear identity for the division within NIST and in the research and industrial communities. Significant progress was made toward these goals this year, but there continued a lack of resources that prevented any program growth. Despite zero total resource growth, we were able to initiate some new efforts and increase our focus. Program changes over the last 18 months had created a much more focused program in chemical engineering, with emphasis on applied thermodynamics, environmental technologies, and separations. A new program in computational engineering was designed to provide a resource to all program areas, and enhance our capability to attract new sources of funds.

Although the Division on the whole seemed to be improving in terms of focus and productivity, there remained a poor outlook for new congressional funding until at least FY94 or beyond. Given the small size of the program it was clear that a major infusion of base program funding was needed to support a growth profile to attain a national level program in a few years. After analysis, a decision was made that CSTL and NIST had insufficient resources to properly rebuild the program. The elimination of the Chemical Engineering Division was announced in September, 1992, with the remaining project areas transferred into the Process Measurements (836) and Thermophysics (838) Divisions in Boulder, and to the Process Measurements Division in Gaithersburg. The new organization includes a new group named "Fluid Systems" in Boulder, which contains the fluid metrology, heat transfer, and applied thermodynamics efforts of the former Properties of Solids and System Dynamics Groups. Another new group, named "Process Separations", merged the separations activities in the former Transport Processes Group, the computational engineering effort, and the process analytical chemistry effort (from Thermophysics). The reactor engineering effort was transferred to Gaithersburg to become part of the Process Measurement Division in the High Temperature Processes Group.

Our heavy reliance on other agency funds continued this year. Overall, the concern over short-term funds versus long-term programs, and the difficulty in focusing so many other agency efforts towards our division goals, were substantially reduced. In particular, we were able to develop external support for two areas of interest: refrigeration for practical superconducting electronics, and process modeling of destruction of hazardous ordnance materials. Internal funds were attracted in support of computational engineering and from the Advanced Technology Program (ATP) to provide modeling support to an ATP winner (in metal organic chemical vapor deposition).

The applied thermodynamics effort has led to a world-class competence in cryocoolers, led by Dr. Ray Radebaugh. This program has been supported by the Air Force and NASA in recent years, with the emphasis being the development of small, reliable refrigeration for cryogenically cooled infrared sensors used in satellite observation of the earth. The work to date has led to several new models for cryocoolers and regenerators, including the only optimization model available to U.S. government contractors. Recently, we have pursued other practical applications of cryocoolers, in particular the pulse tube refrigerator, for which Dr. Radebaugh is one of the leading authorities in the world. While we had expected support from GRI to develop a large scale pulse tube with a thermoacoustic driver (thermoacoustic natural gas liquefier, or TANGL) for liquefaction of natural gas, the funding did not materialize in FY92. Mainly, this was due to a restructuring of priorities within GRI after a funding upset caused by the member companies. We are hopeful that this proposal can be considered again in the future, and we have had some discussions with companies interested in liquefied natural gas depots for refueling vehicles, and the possible use of TANGLs in this application.

Another potential area for application of cryocoolers is in cryogenic and superconducting electronics. It has been documented recently that one of the major technological obstacles to commercializing superconducting devices is the development of low cost, reliable cryocoolers. We have begun research with Tektronix in support of their DARPA program to produce a 10 K cryocooler with sufficient cooling power to cool a superconducting microelectronic circuit. In addition to this work, several proposals were developed this year to establish funding from the NIST superconductivity program and other internal sources.

Several companies interacted with the applied thermodynamics program on a consulting basis this year. As part of our technology transfer efforts, we provided support for Hughes, Ball, Aerojet, General Electric, and others interested in cryogenic refrigeration technology. Applications are now appearing in many areas, such as cooling shielding in the helium system of magnetic resonance imaging systems to reduce boiloff losses, and development of cryogenic surgery instruments to enable currently impossible cryosurgeries. Because of significant interest and research in cryocoolers in Europe and Japan, it is critical that United States manufacturers gain early markets by accelerating development. Our program is well poised to help U.S. industry advance rapidly in this area. Hughes scientists achieved 50 K with a single stage pulse tube this year, and credit our efforts in establishing their laboratory program. We expect to continue close relationships with industrial partners in this area.

With NIST support, our program in computational engineering got off to a strong start this year. To provide an accessible resource and encourage interaction between the different modeling efforts in the division, a computational laboratory was established, including two high-performance workstations, an additional graphics workstation, and a high-end PC system. Modeling projects included development of a powerful new coding approach for finite element analysis of moving boundary systems, and application of the software to modeling metal organic chemical vapor deposition (MOCVD) reactors. Other work included stability studies of a proposed moderator for the NIST cold neutron research facility, finite element analysis of

compressors for cryogenic applications, and various studies in support of other agency programs. Near the end of the year we received a contract from the DoD to provide process modeling of proposed destruction processes for large rocket motors (solid propellants).

In this new effort, Dr. James Welch and Mr. James Hurley will implement commercial simulation software on our workstations, and then work closely with the Joint Services group charged with disposal of the rocket propellant inventory. Our contribution will be a complete chemical engineering analysis of several proposed technologies, and the development of improved models of the chemical reactor steps in the processes. A key concern is the mitigation or elimination of adverse environmental impacts of these large scale chemical disposal efforts. Because the emphasis of the large commercial simulation industry has been on petroleum processing, we plan to work cooperatively with the software companies to develop and implement new modules and new techniques more suited to chemical processing.

Drs. Adele Peskin and Gary Hardin led the effort this year to implement a general finite element moving boundary technique using an object oriented coding approach. The goals were to produce modules that could be incorporated easily into future expanding software libraries. The object oriented approach allows addition of new physical and chemical models or mathematical techniques without disrupting or rewriting the other code. As engineering problems become more complex, this efficiency is critical.

To demonstrate the results of the first year effort, we teamed with SPIRE Corporation, an ATP grant winner, to model a new chemical vapor deposition reactor. The goal of SPIRE's ATP-funded effort is to produce a reactor with feedback control, to improve the yield from wafer processing. Typical materials include GaAs and AlGaAs for photovoltaic devices and other applications. Some funds were provided from the ATP to permit us to visit SPIRE and work with their engineers and scientists to gain a clear understanding of their goals and problems. We obtained data from SPIRE pertaining to the reactor geometry, boundary and operating conditions, and important chemical steps in the reactor. We have already produced preliminary results showing the coupled flow and temperature fields in the actual geometry of SPIRE's reactor, and plan to couple the rotational field and some key chemical reactions very soon. Our results will help SPIRE determine final details of the reactor geometry, and provide insight into the best locations for the sensors that will be used for feedback control. The linkage of ATP grant winners to NIST research through internal ATP funds is an especially fruitful mechanism to produce highly relevant work. Hopefully, these relationships with our programs can continue in the future.

We continue to work with researchers in the Computing and Applied Mathematics Laboratory to develop better models of cryocoolers and regenerators. Because of the unique expertise in modeling and optimization in this area, we have provided support to many private sector efforts, as mentioned above. Current work aims at developing better physical understanding of oscillating flows, so that more accurate descriptions can be incorporated into the models. We expect the research and modeling of oscillating flows to be an exciting area, with little prior

work. Fundamental advances in this area would be of great benefit to the cryocooler research community.

Overall, the computational efforts have moved towards establishing a general resource that can be used to enhance most if not all of our efforts. In addition, the development of a general software tool, such as the object oriented finite element library, should allow us to enhance our research proposals. Already we have developed a modeling proposal to the Intelligent Processing of Materials program (on welding and ceramic injection molding), and will seek other agency support in the coming year. Future budget initiatives, including the Chemical Process Technology initiative, will feature both detailed models and process simulation, and we have established programs well poised to be key contributors.

The fluid metrology program continued this year, with Mr. J. Scott working closely with Dr. G. Mattingly of the Process Measurements Division in Gaithersburg to unify the overall NIST fluid metering program. The emphasis of the work in Boulder has been on further understanding of installation effects in orifice metering. We have conducted extensive studies of the performance of several flow conditioning devices, and the relationship between the meter performance and the flow conditioner type and location, and flow disturbance type and location. The long-term goal is a revision of U.S. and international standards to ensure correct meter performance in all installations. Recent results indicate that the position of the flow conditioner relative to the orifice plate has a more significant impact on the discharge coefficient than the type or location of a disturbance upstream of the flow conditioner. Also, for larger orifice sizes, the position of the pressure measurement taps relative to an arbitrary reference plane has an effect on the discharge coefficient.

Much of the flow conditioner testing to date has been carried out in the 104 mm (nominal 4 inch) line size. Before the standards can be revised to reflect the results from this program and others, some generalization must be made regarding the effects in different line sizes. We are now making measurements in the 52 mm (nominal 2 inch) line size to compare to the earlier results.

Most of the Division's resources in the process separations area are in support of membrane research with a small supporting effort in heat and mass transfer fundamentals. The strength of the world membrane industry derives from the promise of effecting heretofore difficult separations with ease in an energy efficient manner. New membrane materials and new applications are constantly appearing. The Division's program is in two areas: improved gas separations by membrane modification (e.g., composite membranes for higher fluxes; morphology effects by introducing dopants) and prevention of membrane fouling in liquid applications.

Dr. J. Pellegrino completed a DoE-supported program of research on the removal of acid gases from natural gas by selective permeation through immobilized-liquid composite membranes. This included a field study at an operating gas plant. While we could report some successes in the field, it proved to be a difficult way to elucidate the factors affecting performance and we

therefore supplemented the field tests with laboratory tests. This program has now been superseded by a new DoE program for the removal of H₂S. An innovative approach is being taken in which a H₂S- selective, composite catalytic membrane produces soluble polysulphide by oxidation on the permeate side in contact with aqueous sodium hydroxide. Such a process would have many advantages for the natural gas industry. The composite would incorporate an ion-exchange membrane with which we have had extensive experience and continue to refine by microstructure and chemical modification. For example, we recently demonstrated the efficacy of incorporating ionic surfactants in the casting process.

Ultrafiltration continues to play an important role in protein purification in the biotechnology industry and we have for three years been studying the factors which determine membrane fouling in these applications. Drs. M. Ko and J. Pellegrino first characterized membranes in terms of their tendency to form fouling layers. More recently, measurements of streaming potential correlated with measurements of fouling resistance on protein-fouled ultrafiltration membranes have led to an understanding of surface energetics and how protein molecules adsorb and denature. These insights have led to proposals for membrane surface modification by covalent bonding of surface energy modifiers. We are continuing to seek outside support for this work.

In the area of heat and mass transfer fundamentals, we were not able to continue work in process chromatography this year for lack of resources. However, we have identified important directions this work might take and have received informal feedback from industrial contacts reinforcing the appropriateness of such work. In anticipation of future funding possibilities, Dr. M. Jones and Mr. R. Nassimbene made preliminary dispersion measurements on fine glass bead packings using an apparatus developed under DoE funding for packed bed hydrodynamics studies. This apparatus uses a fiberoptic array to detect the spatial and temporal distribution of a fluorescent dye. Results show that this experimental approach could lead to an important new way to characterize process chromatography packings.

In a final component of our process separations program Dr. M. Jones has completed and tested an apparatus for the measurement of mass transfer rates in supercritical fluid extraction from solid matrices. The method uses measurement of the solute uptake in the solvent by *in situ* monitoring of infrared absorption by FT-IR spectroscopy of the supercritical solvent-solute mixture. Working with model systems, the measurements will permit the evaluation of mass-transfer models of the extraction process. Such data are needed in a wide range of potential applications of this technology from food processing to contaminated soils remediation.

**B. Selected Technical Reports
(Chemical Engineering Division)**

1. Fluid Metrology for the Gas Industry

J. Scott and M. Lewis

Orifice meters are used throughout the natural gas industry as flow measurement devices, and are thus critical in the sale of this key energy product. The devices are characterized by a discharge coefficient which relates measured parameters (pressure, temperature, pressure drop) to mass flow. Discharge coefficients are computed using equations defined in national standards. The Gas Research Institute has supported our research to determine how different installation configurations affect the actual discharge coefficient. The goal is to define appropriate installations or flow conditioning techniques that result in performance equivalent to ideal or fully developed turbulent flow in the absence of any disturbances. If general techniques and requirements can be developed for all line sizes, the standards defining meter installation (AGA 3 and ANSI/API 2530) could then be revised, thereby improving the overall accuracy of measurements in the industry.

Our work in fiscal year 1992 has focused on the 52 mm orifice meter. We measured discharge coefficients in fully developed flow with six beta ratios (beta ratio = ratio of orifice plate bore to inside pipe diameter). We term this our 'baseline' configuration. We then tested the effects on discharge coefficients of placing a long-radius elbow 17 pipe diameters (17D) upstream of the orifice plate. This is a common field installation and we think the results can be translated to other piping configurations. We found that with beta ratios less than or equal to 0.55, discharge coefficients were the same as those measured in baseline conditions. For beta ratios larger than 0.55, the discharge coefficients were below baseline values, indicating that flow conditioning was necessary.

We altered the flow between the elbow and orifice plate by placing a flow conditioner 12D upstream of the orifice plate and tested beta ratios larger than 0.66. We used flow conditioners of two types: a bundle of 7 tubes of equal diameter or a bundle of 19 tubes of equal diameter. Tubes in both conditioners were arranged in a concentric pattern and the overall length of the conditioners was at least 2D. The 19-tube flow conditioner worked better than the 7-tube flow conditioner for beta ratios greater than 0.66. When using the 19-tube flow conditioner, discharge coefficients were within 0.25 percent of baseline values over the flow range tested.

There are limited data from other laboratories regarding installation effects in larger line sizes (up to 610 mm). Future work here will include tests similar to those in the 52 mm line, using 104 mm and 152 mm line sizes. We hope to integrate our results with other data to produce general guidelines for the industry.

2. Flowmeter Development for the Space Shuttle Main Engine

J. Siegwarth

The liquid hydrogen fuel and the liquid oxygen (LOX) flows in the ducts of the Space Shuttle Main Engines (SSME) divide into several routes between the supply pumps and the combustion chamber. The efficiency of the engine depends in part on this division. Currently, there is limited control using preset flow resistances to set the flow in the ducts, because of the difficulty of placing satisfactory meters in these short ducts containing many bends. Measurements are also difficult since the fluids are moving at flow velocities up to five times higher than the maximum velocities to which conventional flowmeters are subjected. We are developing some vortex shedding flowmeters capable of measuring the flow in these SSME ducts. Successful measurements of engine performance on NASA's test stand could then be related to actual flows in the ducts, permitting potential improvements in engine efficiency by redesign of the ducts and flow controlling resistances.

We have demonstrated, using water flow to simulate LOX, that a vortex shedding flowmeter can be used to measure flow in the SSME ducts without upstream flow conditioning. Furthermore, these meters can be inserted through an opposed pair of the standard instrument ports used on the SSME ducts.

We previously demonstrated that the meters can measure flow in 51 mm (2") and 58 mm (2.3") engine ducts. The vortex shedding element of these two meters would not give a satisfactory performance but a cylindrical element with a cross slot does. A vortex shedding flowmeter is to be tested in a duct on the SSME engine being studied on the Technology Test Bed at Marshall Space Flight Center. We have provided design specifications and drawings for this meter to NASA, and engine tests are planned in FY 93.

3. Heat Transfer Studies

D. Olson

Heat transfer studies in FY92 involved both experiments and analytical/numerical modeling. In the experimental effort we expanded the capabilities of the high heat flux, hydrogen flow heat transfer facility, and characterized a compact aluminum heat exchanger. A method was developed to predict the performance of compact heat exchangers in which heat conduction in the matrix is significant.

An aerospace manufacturer supplied an aluminum heat exchanger for testing in the flow heat transfer facility. This heat exchanger was a candidate surface for cooling the skin of the National Aerospace Plane. After upgrading the pressure capability of the flow facility to 10 MPa and modifying the high-temperature furnace, this heat exchanger was tested over a variety of flow

conditions and heating rates. The heat exchanger contained 13 rectangular flow channels in parallel, through which high-pressure hydrogen gas flowed to remove the incident heat. Results showed that the heat transfer performance depended on the gas flow rate but was independent of the heating rate.

Compact heat exchangers are often used in situations where one of the fluids has a much higher heat capacity than the other (such as water compared to helium). If the resistance of heat conduction through the solid (matrix) separating the fluids is very low, a simple mathematical relation can describe the heat exchanger performance as a function of the heat capacity, flow conditions, and heat exchanger area. In most situations, the resistance to heat flow in the matrix is large enough to be significant. We developed a finite element model of a general heat exchanger, which included the effect of heat conduction, and coupled it to a flow stream analysis to predict the performance of a compact heat exchanger over a wide range of conditions. The results were incorporated into a simple correlation equation which can be used to predict the performance of compact heat exchangers without ignoring the effects of matrix heat conduction.

4. Neutron Moderator LH₂ Demonstration System

J. Siegwarth, M. Lewis, and D. Olson

The Reactor Division of the Materials Science and Engineering Laboratory (MSEL) operates a 20 MW research reactor in Gaithersburg. A cold D₂O ice moderator is used to provide a source of thermalized long-wavelength neutrons. This Cold Neutron Research Facility has enabled a variety of physics and materials science research. The flux of neutrons at the wavelength of interest can be enhanced by further cooling of the neutron source moderator. Increasing the cold-neutron flux can improve the resolution or reduce the measurement time for many experiments and measurements. The Reactor Division has proposed a liquid hydrogen (LH₂) moderator to significantly enhance the flux of neutrons at the desired wavelength. Such a moderator must operate in a closed system with an estimated heat flux of 1 kW. In addition to numerical studies of stability described later, the Chemical Engineering Division constructed a full-scale LH₂ mockup system to test the behavior of the proposed moderator.

We completed a test system and initiated experiments this year. The main components duplicated in our system are the spherical LH₂-filled annulus which is the moderator, and the coaxial gas-liquid recirculation line. In the actual system, the sphere and the lines will be fabricated from aluminum and connected in a closed loop to a helium-cooled condenser. Our test system duplicates the aluminum lines but uses a glass sphere about 450 mm in diameter so that the bubble fraction and dynamic behavior in the sphere may be observed directly. While the cold neutron source will be heated by gamma radiation from the reactor, we designed the test system to be heated with a resistance heater wound inside the annular space. Finally, we used a constant head device and a pump to deliver liquid to the moderator, and the gas produced was allowed to vent at a controlled pressure, rather than condensing in a closed system.

Tests thus far have shown that the LH₂ circulation is self regulating and stable at heat inputs from 500 to 1500 watts. The tests have shown also that the gas volume of the moderator caused by the heat flux is well under the maximum acceptable 20%. We are currently investigating problems associated with restarting the circulation following flow stoppage. A modification to the experimental procedure, in which the LH₂ will be brought into the bottom of the moderator container, has been designed to speed up the restart of the circulation and will be tested..

5. Free Convective Cooling of NASA Engine LH₂ Pump

J. Siegwarth and M. Lewis

Prior to firing the engines of a cryogenic liquid fueled rocket, the feed lines to the turbopumps must be precooled to near the operating temperature. The cooling procedures for the feed lines differ for liquid hydrogen (LH₂) and liquid oxygen (LOX). The LOX lines are cooled by convective processes (passive recirculation) within the LOX duct, while the LH₂ lines are cooled by discharging the gas formed in the cooling process by a vent valve at the turbo pump.

For the next generation of launch vehicle, the National Launch System (NLS), NASA wants to use passive recirculation in the LH₂ lines. To test the feasibility of using passive recirculation in the NLS, we built a 1/5th scale version of the NLS LH₂ duct at NIST Boulder. This duct had glass sections for viewing the flow pattern of the LH₂ and bellows connections to allow the angle of a horizontal section to be varied from level to 20° down. A heater was clamped to the termination of the duct to represent the turbopump. Heat could be applied to simulate the heat leak to the turbopump. Vent valves could be closed to pressurize the tank to suppress boiling in the duct before the pump is started. Under low heat leak conditions to the duct, this suppression lasted more than a minute.

We ran two tests with this apparatus. The tests proved passive recirculation in LH₂ worked so well, even under conditions of a poor insulating vacuum, that no further tests were deemed necessary. As a result of our test, NASA has built a full scale test system at Marshall Space Flight Center to test passive recirculation in the full scale duct.

6. Cryocooler Development for Superconductivity Applications

R. Radebaugh and P. Bradley

We have started working with Tektronix Corp to develop a superconducting device and a cryocooler, as part of a 4-year program to assist with the development of a no-moving-parts refrigerator. This refrigerator will be designed to reach 10 K for the cooling of niobium nitride superconducting devices. This concept uses the thermoacoustically driven orifice pulse tube refrigerator recently developed and patented by NIST and Los Alamos National Laboratory. We

will design and test various staging concepts to reach 10 K, first with a 100 Hz driver and then with a 400 Hz driver. The higher frequencies lead to a smaller package, which is one of the program goals.

In FY92 we determined the optimum operating pressure for the system to achieve 10 K in a compact package. We have also completed preliminary designs of the regenerators and the pulse tubes that are required at each stage, and have identified problem areas. Low porosity structures with high heat capacities are very important for the third and fourth stage regenerators. A test apparatus has been conceptually designed and detailed drawings are now being done. We plan to use a two-stage commercial Gifford-McMahon refrigerator, capable of providing about 2 W at 10 K and tens of watts at 40 to 50 K, as part of the test device that will test out various regenerator stages and be able to measure their losses at the operating frequency of either 100 Hz or 400 Hz.

7. Development of Compressors for Cryocoolers

R. Radebaugh and E. Marquardt

The work discussed here is a continuation of our effort to develop long-life cryocoolers for satellite applications, which has been going on with NASA/Ames since 1983. These coolers would be used to cool infrared sensors used in studies of the ozone hole and greenhouse effect. The pulse tube refrigerator has no moving parts at the cold end; the compressor is the only component with a moving part. Recent work at the University of Oxford showed how to use flexure springs to support a piston inside a cylinder with no touching, using a clearance seal of about 15 μm . A linear-resonant motor produces the reciprocating motion of the piston inside the cylinder to produce the required pressure oscillations needed by the pulse tube refrigerator. Placing two of these compressors back-to-back eliminates most of the vibration from the reciprocating motion.

The compressor is designed to be a laboratory model that is flight-like but uses some simplifications to reduce the costs required for a flight-qualified model. The compressor will become part of a complete two-stage pulse tube refrigerator for tests by NASA/Ames.

We have developed all the design equations in FY92 for these linear-resonant compressors and have shown how to scale these to various sizes. The present model is designed for a 20 cm^3 swept volume, a 45 Hz operating frequency, an average pressure of 2.0 MPa, and a pressure ratio of 1.5. It will deliver 360 W of PV power at an efficiency of 83%. Layout drawings and many of the detailed drawings have been completed. We are incorporating a new design for the flexure springs, which are as much as an order of magnitude stiffer than the Oxford design, in the radial direction. The increased stiffness will eliminate touching contact even for slight misalignments. The detailed design of the flexure springs for a ten-year life time required a nonlinear finite element stress analysis of the spring at full extension. Some of these flexure

springs were manufactured for us in FY92 and measurements of the radial and axial stiffnesses will be made and compared with our calculated values before proceeding to have parts made for the rest of the compressor. We are presenting a paper on the design equations and scaling laws for these very efficient linear compressors at the 7th International Cryocooler Conference in November, 1992.

8. Development of New Regenerator Materials

R. Radebaugh, W. Rawlins (Univ. of Colorado), and K. Kapkin (Univ. of Colorado)

This program has two parts: (a) the measurement of regenerator performance with different materials and configurations for the temperature range of 77 K to 300 K, and (b) the development of new materials and configurations for regenerators operating at temperatures below 40 K. These regenerators would be used in cryocoolers such as the Stirling, Gifford-McMahon, or pulse tube types. In the first category we have refined the measurement techniques for determining regenerator ineffectiveness and are able to get very reproducible results. This work is in collaboration with the Chemical Engineering Department of the University of Colorado. The hot-wire anemometry techniques developed for these cryogenic measurements represent state-of-the-art advancements. In FY92, measurements were made on stainless steel screen regenerators. We have compared two such regenerators; one of which was made with all one mesh size, while the other was made with three different mesh sizes. In the second case, the coarsest mesh is used for the warmer one-third and the finest mesh is used in the colder one-third of the regenerator. Our modeling predicted that there would be no difference in the performance, but many cryocoolers are being made with graded screen mesh with the expectation that it improves the performance. Our experimental results obtained in FY92 have shown that there is indeed negligible difference between these two arrangements.

We have also been working with the University of Colorado in the development of new regenerator materials. Methods for depositing various rare earth alloys with high heat capacities (Er_3Ni is one example) onto substrates such as stainless steel or nickel screen have been explored. Evaporation and the painting of colloidal suspensions followed by sintering have been tried with reasonable success. An apparatus for measurement of specific heat in the temperature range of 4 to 40 K has been designed and constructed, and will be fully instrumented in the coming year. The apparatus will use the thermal relaxation method of specific heat measurement. A silicon-on-sapphire thermometer and heater substrate will be used to hold the samples with a small amount of thermal grease. Thus, the samples can be changed quickly with no need for disturbing the thermometer and heater assembly.

We have collaborated with the NIST Metallurgy Division regarding the rare earth materials, and expect additional interactions in this area in the future.

9. Studies of Membrane Morphology in Gas Separations

J. Pellegrino, D. Wang (Univ. of Colorado), P. Giarratano, M. Yetzbacher, and T. Cirbo

Membrane separation is defined as the use of an interfacial, non-partitioning phase (usually very thin) to provide a selective molecular barrier between two process phases. In gas separations, mixtures of permeant gases are separated or purified by the imposition of a partial pressure gradient across the membrane. In vapor separations, either condensible components exist in a gas stream or a liquid mixture is evaporated through the membrane. Currently, membranes are being introduced into O₂/N₂ separation, H₂ recovery, natural gas purification, dehydration of alcohols and other organic solvents and removal of organic contaminants from air and water streams.

Our research has focused on studying a phase-separated, ion-exchange polymer polyperfluorosulfonic acid (PFSA). Our main application area is gas separations (H₂S, CO₂, CO, H₂, CH₄, O₂). In vapor separations we have studied the same polymer for separation of polar and non-polar organics, NH₄ and water dehydration. Our programs have included applications testing, process system analysis and design, transport process modeling and polymer microstructure science. In the past year we have concentrated on the structure-transport property relationships which result from casting thin films from PFSA polymer. This is an important issue for commercial use of this potentially very versatile polymer in separations. Economics require very thin films which can be coated on inexpensive porous supports. So far our experiments have shown that coated, thin films perform less satisfactorily than commercially available films of PFSA. We have attributed this to morphology effects which we are now trying to better understand. A major goal is to provide a rational model for manipulating coated, polymer films to achieve desired separation properties.

In collaboration with the University of Colorado Center for Separations Using Thin Films, we have developed several novel ways of changing the supramolecular morphology of films cast from PFSA polymers. These techniques include adding ionic surfactants to the casting solution, as well as techniques for post treatment of the films. In addition to the direct effect of adding surfactant to a casting solution, we have also initiated a systematic study of the effect of solvent, composition and casting time and temperature. We now believe that the morphology of the PFSA films contains three phases: an ionic cluster phase, an amorphous phase and a crystalline phase. These phases are distributed throughout the film, with the amorphous phase most likely the continuous phase. The film formation and post-treatment conditions can change the relationships between these phases and their intraphase condition. An important example of the former is the size of ionic phases, and of the latter is the free volume present in the amorphous phase.

Using a combination of multi-component gas permeation measurements (CO₂, CH₄, and H₂S), water absorption measurements, differential scanning calorimetry and small angle x-ray

scattering, we are developing support for our three phase viewpoint. For example, we have shown that even though films have higher water content (and presumably larger ionic clusters) they do not necessarily permeate gases faster. These results argue for the "rate-limiting" role of the permeation through the regions between ionic clusters. Treatment of both commercial and cast films with plasticizers (mediocre solvents for the polymer) has allowed us to develop free volume in the intercluster (amorphous) phase without disrupting the crystallinity required for mechanical strength. These films show enhanced permeation rates.

10. Protein-Surface Interactions on Polymeric Ultrafiltration Membranes

M. Ko and J. Pellegrino

In various membrane separation applications, process streams are encountered that contain biological and larger organic materials. A phenomenon known as "membrane fouling," caused by adhesion of these materials onto the membrane surface, has detrimental effects on performance, including drastic and irreversible reduction in flux and change in selectivity. It is a generic and major problem in membrane separation. Our research during FY92 was aimed at a better understanding of protein-membrane interactions at the interface and the development of a low-fouling membrane incorporating features suggested by this understanding.

Proteins in water interact with and adhere to a solid surface. Fouling processes have been characterized by the long- and short-range interactions and solvation among solutes, water, and the membrane surface. As proteins approach the surface, they first experience long range interactions (dispersion, electrostatic, steric hindrance, and polymer bridging) with the membrane surface. Protein adsorption is thought to occur in several simultaneous steps: (1) charge redistribution in overlapping electrical double layers of protein and solid surface, (2) dehydration of the solid surface and protein, and (3) structural rearrangement of the adsorbed protein molecule. The irreversible nature of the adsorption is due to this structural rearrangement of the adsorbed protein upon dehydration of the surface and protein. Our study concluded that solvation is the most important parameter among these interactions. Irreversible fouling is reduced if the proteins are maintained in their original conformation (hydrated and unbound). Negative surface charges (electrostatic repulsion) also reduce adsorption. The total energy profile of the protein-surface interaction suggests that it would also be important to lower the membrane surface energy. Our research on fouling provides fundamental insights on how to tailor the membrane surface to lower the irreversible protein adsorption.

To demonstrate this, we are developing a low fouling membrane by surface modification of a commercially available tough membrane (carboxylated polysulfone) which has controlled pore characteristics. The membrane treatment technique involves attachment of extremely hydrophilic tails to the surface by covalent bonding. The attached hydrophilic tails regulate protein collision onto the interface by steric hindrance repulsion at their tip, and therefore lower protein loading. When spacing between the tails is smaller than the protein molecules, the proteins do not interact

directly with the surface. The hydrophilic nature of tails creates a water-buffered layer which results in a hydrated protein layer where the adsorbed proteins may stay in their native form during filtration. Our first surface-modified membrane (reacting a glucoseamine and carboxylic acid group on polysulfone) showed promising reduction of fouling. Our continued work will provide scientific insights into the interfacial mechanisms and should lead to more economical separations for US industries.

11. Mathematical Modeling of Transport Processes

A. Peskin and G. Hardin

Numerical software for simulating and analyzing engineering problems of fluid flow with associated heat- and mass-transfer finds increasing use as techniques evolve to model more complex physical situations and computing costs continue to fall. It is now often feasible to model complex transport physics and chemistry completely by numerical methods, even when unifying theoretical descriptions are not available, and to use these to plan and interpret experiments. Consequently, computational fluid-dynamics software is an increasingly important tool for understanding the complex physical environments that arise in engineering applications.

We have developed a highly flexible numerical library to model transport phenomena in a wide range of applications. This software employs the finite element method and is well suited to problems involving arbitrary geometries. A key feature of our software is the capability to address problems with moving boundaries such as interfaces. The software design is object oriented, allowing for efficient and rapid implementation of modular code to address the requirements of a specific problem, which then becomes part of a growing tool set. This is especially important in a research environment, where problems involving complex physics are often the rule and for which accurate models may not be available. Sample applications we have tackled to date include tracking the growth of an electrode during electrochemical deposition (including coupled fluid dynamics, chemistry, and electrical-potential fields) and simulating chemical vapor deposition on a rotating substrate for the design and characterization of a commercial reactor.

Currently, we are adding features to the code that are particularly relevant to chemical-engineering applications, such as a generalized structure for implementing a large number of chemical reactions with finite kinetics. We will also expand the code to model interfacial physics such as tension, interfacial-tension-driven flow, and interfacial heat- and mass-transfer. We also plan to implement expanded capabilities to model highly-deforming surfaces and the break-up of a free surface, parameters often encountered in chemical processing.

We will apply these capabilities to investigate the manufacture of supported polymeric membranes. Current membrane fabrication techniques are poorly understood, and are subject to high failure rates. A fundamental investigation will pursue the mechanism and conditions that

lead to defects. This will provide critical understanding to allow the manufacture of thinner membranes with greater mechanical integrity. The outcome would be more productive membranes and more energy- and cost-efficient chemical separations modules.

The basic strategy of this project is to use a highly modular, object-oriented software design to quickly and efficiently model physical processes important to the process separations research program. In developing capabilities to model specific process separations applications, we will be adding to an expanding unified set of tools which is expected to grow in both the breadth and complexity of physical situations it can model.

12. Supercritical Extraction from Porous Matrices

M. Jones and M. Wood

The advantages of using environmentally benign, supercritical fluids as solvents for extraction are well known in applications such as hydrocarbon, chemical and food processing and contaminated soil treatment. Improved transport properties, new and improved products, and the ability to remove the solvent completely after extraction, are often quoted. For design of commercial scale processes, data and models are required to predict the rate of extraction and thus ultimately the contact time. The desired extract may reside in a porous matrix and be held mechanically or bound by physical adsorption or chemisorption. The kinetics of desorption may be masked by mass transfer limitations both internal to the matrix and by external hydrodynamically determined mass transfer, the latter being characteristic of the state of aggregation of the raw material.

Our research aims at developing mass transfer models of the extraction process. To do this it is best to perform well characterized and controlled experiments on a few model systems. Once these systems can be understood and modeled mathematically, we can proceed to the more interesting real world systems. Central to the modeling effort is the proper representation of the thermodynamic driving force in addition to the convective and diffusive processes.

To carry out the experimental program we have constructed an apparatus in which model matrix-solute systems can be studied. The desired rate parameters can best be obtained from the dynamics of extraction of matrix particles in a zero gradient extractor/reactor with variable hydrodynamics. We monitor the dynamics *in situ* by observing infrared spectra in a transmission cell fiberoptically coupled to a remote Fourier Transformed Infrared (FT-IR) spectrophotometer.

In the previous year we were able to test out the FT-IR measurements in a specially constructed high pressure transmission cell. Some improvement in optical throughput was achieved this year. We also completed the extractor apparatus and made preliminary experimental runs with a model system consisting of microporous silica particles saturated with hydrocarbons. Extraction

experiments were carried out with the particles held in a zero gradient extractor fitted with a variable speed impeller. Results are being analyzed.

13. Neutron Moderator Hydrogen System Stability Studies

G. Hardin, P. Giarratano, and M. Jones

The Chemical Engineering Division was asked to provide pre-design verification studies for an improved cold neutron source currently under development by the Reactor Division. The novel design uses liquid hydrogen in a spherical annulus fed by natural circulation from a helium-cooled condenser in a completely passive system i.e., no moving parts. Experimental verification is described elsewhere. This report deals with a parallel stability study carried out to identify possible regimes of unstable operation to be avoided by proper design.

The proposed system is essentially a two-phase natural-convection loop to provide liquid hydrogen to a spherical annulus through which the neutron beam would pass. The key elements are the annulus, or moderator chamber, in which the incident neutrons are thermally equilibrated, a condenser to re-liquify hydrogen boil-off from gamma ray heating, liquid supply and concentric vapor return lines and a gas reservoir to provide a buffer volume into which the hydrogen could expand for containment in the event of a cooling failure. The cold-neutron beam would emerge from a hydrogen-free window on one side of the annulus. This configuration is expected to provide a stable, well-characterized beam. The purpose of the modeling work was to explore the possible steady operating states of this design, and to analyze these states for stability. A thirteen variable process model was developed to describe the system.

The steady-state analysis uncovered opportunities for improved operation and a number of potential problems that could occur with even relatively small excursions from the design power-level. The model showed that, at reduced power, the annulus would flood pushing liquid hydrogen into the vapor-return line, while, at elevated power, the annulus became severely depleted of liquid, greatly compromising its ability to condition the neutron beam. Exploration of different configurations revealed the condenser to be the key component in establishing the operating pressure, and the total hydrogen inventory to be a key parameter affecting how well the system would behave in the event of a power excursion. It was determined that reducing the operating pressure would allow a reduction in the size of the buffer volume and a consequent reduction of the hydrogen inventory. The net effect of these design changes could narrow the variability of the liquid fraction in the annulus, greatly improving the consistency of operation over even a fairly wide range of power.

The stability analysis is near completion, and tools are now available for continued iteration of the design as needed.

14. Chemical Reactor Engineering

J. Welch and J. Hurley

We have been working for the past several years to develop advanced technology for the reactor component of an Air Force chemical laser system. A number of engineering and technical issues must be resolved for the overall system to be deployed. The reactor is designed to produce oxygen in molecular form but in an electronically excited state, the so-called singlet delta state. Singlet oxygen is used to carry chemical energy in the laser flow duct and transfer it to iodine to create the species used in the lasing transition. The overall system is known as the Chemical Oxygen Iodine Laser or COIL.

In the COIL reactor, a reaction takes place between gas-phase chlorine and aqueous ionic species, producing oxygen in stoichiometric quantities to the chlorine reacted. The ionic reactants are formed by the reaction of hydrogen peroxide and potassium hydroxide in aqueous solution, to form the O_2H^- ion. The resulting mixture is called basic hydrogen peroxide or BHP, and is marginally stable when stored at low temperature (250 K). Some issues surrounding the decomposition of the reactants have been addressed this year.

The decomposition of BHP results in the evolution of oxygen gas in the ground state. In the reactor system, this is detrimental due to 1) loss of reactant, and 2) production of foam from the evolving gas. We studied the decomposition of BHP and hydrogen peroxide solutions with and without trace amounts of iron (Fe^{+2} , Fe^{+3}). It was suspected that iron contamination was leading to various failures in existing COIL research systems. We found that the state of the iron contaminant had no effect on the decomposition rate, and that the rate increased with increasing iron concentration. It was determined that the addition of the chelating agent ethylene-diamine-tetra-acetic acid, EDTA, in stoichiometric quantities relative to the iron, inhibited the decomposition of BHP. Addition of excess EDTA did not further suppress decomposition.

The overall performance of COIL depends in part on the yield of singlet oxygen from the reactor, as well as the efficiency of chlorine utilization. Much of our effort has been to understand the factors influencing the yield of singlet oxygen, and suggest improvements to the reactor and other systems. Because singlet oxygen is deactivated to ground state by both gas-phase homogeneous and gas-solid heterogeneous reactions, an optimal reactor design must involve tradeoffs between reactor volume or surface area and singlet yield, because increases in the volume or area increase both the generation and deactivation term. The situation is analogous to the classical chemical engineering problem in reactor design when there are undesirable side reactions which consume product. In addition to these overall considerations, there is much evidence that the reaction between dissolving chlorine and the production of excited oxygen occurs essentially at the liquid-gas interface. We constructed a reactor in which the liquid surface was continually regenerated by convection in the liquid phase, and observed that the overall reaction rate of singlet oxygen was maintained at the characteristically high value

observed initially. Without surface renewal, the production of singlet oxygen falls off markedly after an initial maximum.

BHP is typically maintained at 273 K or lower prior to contacting with chlorine. However, the reaction to produce oxygen is highly exothermic, and it is likely that significant heating of the surface reacting layer occurs. It is desired to characterize the temperature rise since the kinetics will be affected by the temperature, and models of the system depend on accurately predicting the kinetics. We constructed an apparatus in which we suspended droplets of diameters from 500 to 2000 micrometers on a glass filament. A thermocouple bead of diameter 15 micrometers was positioned in the center of the droplets, and connected to a real-time data acquisition system. Using this system, we have made initial measurements of the droplet temperature versus time, with and without chemical reaction occurring. Further experiments and analysis are planned to permit measurement of kinetics and heat transfer, so that film temperature profiles may be predicted for full-scale reactors.

We have continued our modeling efforts this year, and developed an efficient model to calculate the steady-state axial and radial concentration profiles for laminar flow in a tubular reactor with wall deactivation of the gas phase products. The model is useful to predict the performance of calibration systems, as well as predicting the loss of singlet oxygen to ground state in the duct between the reactor and the lasing cavity. As part of our ongoing effort to develop alternative heterogeneous reactor schemes, we developed an unsteady-state, one dimensional model for the first order heterogeneous reaction in a plug flow reactor. This model is also useful to predict the performance of reactors utilizing stationary liquid films.

Another key activity in the reactor engineering program has been to contribute to the solution of pressing environmental issues surrounding the disposal of hazardous wastes. In addition to COIL, we are interested in the role of electronically excited oxygen in novel oxidation pathways, which may be useful in the destruction of otherwise refractory compounds. Future work may address the applicability of excited molecular oxygen to waste treatment and other chemical processing applications.

This year we initiated a new program funded by the Joint Ordnance Commanders Group (JOCG), a DoD Joint Services committee charged with the disposal of very large quantities of ordnance waste. We will undertake to model several proposed technologies for the destruction of large rocket motors. Although there are over 300,000 tons of solid propellants in inventory that must be destroyed, there is a lack of available technologies for the disposal effort.

15. Hydrodynamic Effects in Packed Bed Separation

M. Jones and R. Nassimbene

In chemical process technology the packed bed is one of the most frequently used structures for effecting separations such as in adsorption, ion exchange, and process chromatography. The quality of separation obtainable depends on several factors including bed uniformity, flow distribution, particle size, mass transfer effects, and adsorption. When the bed is not isothermal, or when density gradients arise from solute concentration changes, buoyancy forces may further influence the quality of separation. Dispersion is an indicator of the quality of separation and we have recently completed a series of measurements of this quantity on model packed beds. Our experiments have allowed us to investigate some of the factors affecting the hydrodynamical contribution to dispersion.

In one series of measurements we have measured dispersion in a series of uniform isothermal beds with varying particle size and flowrate. A new technique has been used in which the time-resolved response and spatial variation of a tracer dye can be observed by a fiberoptic array. Thus, the dispersion coefficient can be obtained from both the residence time distribution and the statistics of the response times observed at individual fibers. In a second series of measurements, we have studied nonisothermal operation and the influence of buoyancy forces on dispersion. Using the fiberoptic array, we can also map flow distribution and interpret it in terms of secondary flow structures. These measurements help to set limits to operating variables in order to remain in a region of low dispersion.

In future work we wish to use the techniques we have developed to characterize the dispersion attainable in commercially available and novel packings for process scale chromatography. This is particularly important in separations encountered in biotechnology, where scale-up is often a matter of empiricism, and a systematic approach would be welcome. This is also a very active area for new developments in packings as the quest continues for higher throughput without sacrifice in the quality of separation or the useful lifetime of the packing.

**C. Outputs and Interactions
 (Chemical Engineering Division)**

1. Publications

- Bradley, P.E., Radebaugh, R., and Gary, J., "Comparison of Regenerator Performance in a Vuilleumier Refrigerator with a Third-order Numerical Model," Adv. Cryo. Eng. 37B, 1085-1093 (1991).
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- Scott, J.L., Sindt, C.F., and Lewis, M.A., "Flow Conditioner Location Effects in Orifice Flowmeters," Tech Note 1356 (1992).
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- Siegwarth, J.D. and Lewis, M.A., "Vortex Shedding Flowmeters for SSME Ducts," NASA Conference Publication 3174, 1, 217 (1992).
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- Welch, J.F., Hurley, J.A., Glover, M.P., Nassimbene, R.D., and Yetzbacher, M.R., "Unsteady Laminar Flow in a Circular Tube: A Test of HERCOL (Hermitian Collocation) Computer Code," NISTIR 3963 (1992).

2. Talks

- Hardin, G., "Nonlinear Stability of Thin Liquid Films," AIChE Annual Meeting, Los Angeles, CA, November 1991.
- Ko, M., "Streaming Potential Studies of BSA Protein Interactions with Porous-Polymer Membrane Surfaces," AIChE Annual Meeting, Los Angeles, CA, November 1991.
- Ko, M., "Protein-Surface Interactions and Their Effects," Seventh Symposium on Separation Science and Technology for Energy Applications, Knoxville, TN.
- Pellegrino, J., "Poster: Surfactant-'Doped' PFSA Membranes for Gas and Vapor Separations," Engineering Foundation Conference on Separation Technology, Kona, HI, October 1991.
- Pellegrino, J., "Ion-Exchange Membranes for Organic Separations," Membrane Technology and Planning Conference, Boston, MA, November 1991.
- Pellegrino, J., "Overview of NIST Research in Ion-Exchange Polymers, Membrane Fouling and the Formation of Thin Film Composite Membranes," An Intragency Consortium on Desalination and Membrane Research Planning Meeting, Boulder City, NV, April 1992.

Pellegrino, J., "Acid Gas Separations from Natural Gas with Enhanced Transport-Ion Exchange Membranes: Field Test Results," Natural Gas Research and Development Contractors Review Meeting, Morgantown, WV, May 1992.

Pellegrino, J., "Cast, Surfactant-'doped' PFSA Membranes for Gas and Vapor Separations: Morphology Investigations," North American Membrane Society Annual Meeting, Lexington, KY, May 1992.

Pellegrino, J., "Reactive Membrane Processes," Short Course, 1992 North American Membrane Society Annual Meeting, Lexington, KY, May 1992. Invited

Pellegrino, J., "Gas Separation Using Ion Exchange Membranes for Producing Hydrogen from Synthesis Gas," 12th Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, DoE, Morgantown, WV, September 1992.

Radebaugh, R., "From High C to Low T: The Contribution of Music to Cryogenics," Inaugural Meeting of the Rocky Mountain Chapter of the Cryogenic Society of America, Denver, CO, March 30, 1992. Invited

Radebaugh, R., "Pulse Tube Refrigeration," NIST/Boulder Colloquium Series, Boulder, CO, June 5, 1992, Invited

Radebaugh, R., "Thermoacoustics and Pulse Tube Refrigeration," University of Colorado, Physics Dept. Colloquium, Boulder, CO, September 30, 1992, Invited

Radebaugh, R., "Survey of Heavy Fermions for Thermoelectric Cooling," Workshop on Thermogenic Cooling, U.S. Army Night Vision Laboratory, Ft. Belvoir, VA, September 17 1992.

Scott, J.L., "Transmission Measurement Committee Meeting of the American Gas Association," May 1992, Talk included Results of Long-term Transducer Study, Review of Technical Note 1352 and Description and Tour of Flow Facility.

Scott, J.L., "Technical Advisory Committee Meeting of the Southwest Research Institute," San Antonio, TX, Results of 1991 Research, April 1992.

Siegwarth, J.D., "Vortex Shedding Flowmeters for SSME Ducts," Advanced Earth-To-Orbit Propulsion Technology Conference, May 1992.

3. Cooperative Research and Development Agreement (CRADAs) and Consortia

None

4. Patent Awards and Applications

Dutta, B. and Sikdar, S., "Manufacture and Use of a Composite Membrane for Separating Azeotropic or Close-Boiling Mixtures," (Awarded November 1991, 89-028)

Pellegrino, J., Ko, M., and Marko, P., "Coating the Inside of Microporous Hollow Fibers with Polyperfluorosulfonic Acid (PFSA) Film-Forming Polymer," (Submitted January 1990).

Sikdar, S. and Lund, D., "Method for Making Single Crystals," (Awarded April 1992, 88-022)

Szlag, D. and Giuliano, K., "Aqueous Two-Phase Protein Extraction," (Awarded March 1992, 90-006)

5. SRM Activities

None

6. SRD Activities

NIST/GRI Orifice Meter Research Database (new)

7. Calibrations

State of California
Foxboro Company
Hoffer Flow Controls

8. Committee Assignments

J. Hord

International Association for Hydrogen Energy
Committee on Hydrogen Safety (Chair)
9th World Hydrogen Energy Conference Safety Session (Chair)
American Institute of Chemical Engineers
National Research Committee (Past Chair)

M.C. Jones

AIChE Area 1f, High Pressure Committee
AIChE Area 7b, Heat Transfer Mechanisms Committee

J. Pellegrino

National AIChE Separations Division, Director
Separations Division liaison to DIPPR
CU Center for Separations with Thin Films-Industrial Advisory Board
Interagency Consortium on Desalination and Membrane Separation Research

R. Radebaugh

Advisory Board of International Cryocooler Conference

J. Scott

Technical Advisory Committee for the GRI Metering Research Facility at Southwest
Research Institute
Transmission Measurement Committee of the American Gas Association
North American Ad Hoc Orifice Meter Expert Committee

J. Welch

AIChE Equipment Test Procedures Committee

9. Editorships

J. Pellegrino

Gas Separation and Purification Journal (Founding Member, Editorial Board)

R. Radebaugh

Cryogenics (Editorial Board)
American Institute of Physics, Modern Instrumentation and Measurements in Physics
and Engineering (Editor-in-Chief)

10. Seminars

None

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

None

12. Other

a. Academic Appointments

J. Pellegrino

Adjunct Professor, Colorado School of Mines

III. Chemical Kinetics and Thermodynamics Division (833)

Sharon G. Lias, Chief

A. Division Overview

Chemical kinetics and chemical thermodynamics are concerned with two aspects of chemical stability. Thermodynamics treats the energetics of chemical transformations with the goal of determining the feasibility or spontaneity of a given process, and perhaps more important, of knowing the equilibrium yields to be expected for a process. Chemical kinetics is the study of the rates of chemical reactions, the factors which influence those rates, and the detailed mechanisms of the reactions. An understanding of the kinetics and thermodynamics of any process involving chemical change is necessary to predict and control the process. A detailed understanding of the energetics and mechanisms of chemical change is at the very heart of chemistry, and constitutes an important goal of science. Societal applications of data from chemical thermodynamics and kinetics are numerous and diverse. These include understanding and modeling combustion processes, unravelling the complex effects of pollutants on the earth's atmosphere, and predicting equilibrium properties of processes of interest to technology.

The Division is administratively divided into three groups, the Experimental Chemical Kinetics Group, the Kinetics Data Centers Group, and the Chemical Thermodynamics Group. The work of the latter Group includes both experimental and data evaluation activities in the area of thermodynamics. There is a significant degree of overlap between the technical activities of the three Groups, with individual scientists often carrying out collaborative assignments which cross Group lines.

The programs of the NIST Chemical Kinetics and Thermodynamics Division include experimental measurements of kinetic and thermodynamic quantities, the development of measurement techniques and methodologies, the development and certification of Standard Reference Materials (SRMs), and the generation of databases of high quality evaluated numeric data, Standard Reference Data. The latter activity, which is carried out in four Data Centers within the Division, provides the most important mechanism for disseminating Division outputs to the technical community. The tie between the experimental programs and the work of the Data Centers is strong with many Division scientists actively engaged in both experimental and data evaluation projects. The considerable breadth of ongoing experimental activities in the Division ensures that the expertise and insight needed for reliable data evaluation is available. The theoretical expertise available in the Division supports both experimental and data evaluation work.

Research activities are driven largely by the needs of the various communities which are served by Division programs, with the Chemical Kinetics and Thermodynamics Division serving as a technical resource for a wide range of external programs. These activities in support of other programs are an integral part of our mission, and a key means of applying our scientific expertise

to the solution of industrial, environmental, defense, and energy-related problems. In 1992, 31% of Division research was supported by other agencies, notably including the Department of Energy (DoE), the National Aeronautics and Space Administration (NASA), the Environmental Protection Agency (EPA), and the Department of Defense (DoD). Another 27% of Division work was supported by the Standard Reference Data Program (SRDP). The four Division Data Centers (Chemical Thermodynamics, Chemical Kinetics, Ion Kinetics and Energetics, and Mass Spectrometry) which are sponsored by the SRDP operate under the authority of the Standard Reference Data Act of 1968 which makes it a part of the National Institute of Standards and Technology (NIST) mission to collect, compile, critically evaluate, and disseminate evaluated technical data. Work carried out in this Division comprises an important segment of that program, with databases originating in this Division accounting for 72% of databases distributed by SRDP in 1992.

Users of Division databases are 65% industrial, 14% academic, 13% government (federal, state, and local), and 7% other (including foreign) laboratories. A list of industrial users of Division database products shows the breadth of usefulness of Division products to American industry, with users including companies from the chemical, pharmaceutical, food and beverage, rubber, petroleum, communications, aerospace, microelectronics, and computer industries, as well as many hospitals, environmental laboratories, and other businesses. Government users include state and local law enforcement agencies, drug testing laboratories, and all the federal government agencies having laboratory facilities (Agriculture, Food and Drug, Fish and Wildlife, Federal Bureau of Investigation, National Institutes of Health (NIH), EPA, DoE, etc.).

The focus of both experimental and Data Center programs in the Division is largely determined by national needs in areas where chemical kinetics and thermodynamics data are important. At the present time, most of the on-going work, including both experimental and data evaluation activities, is relevant to **environmental problems and technology, energy, industrial processes, and/or analytical chemistry.**

The Division has a long history of involvement in projects concerned with **atmospheric environmental problems.** Work on effects of man-made chemicals on the earth's ozone layer began in our laboratories in the early 1970's, and has continued to the present. Division members hold important leadership positions in relevant national and international organizations, such as the panel which provides the definitive recommendations of data for modeling stratospheric chemistry, NASA's Upper Atmosphere Research Program, and the Scientific Steering Committee of the International Network for the Detection of Stratospheric Change.

The experimental program of the Division's atmospheric kinetics laboratory involves the measurement of the gas phase kinetic parameters for chemical reactions important in atmospheric chemistry, with emphasis on processes which relate to the fate of natural and man-made trace gases in the troposphere, their chemical role in the stratosphere, and problems surrounding the depletion of stratospheric ozone. Both the Chemical Thermodynamics Data Center and the Chemical Kinetics Data Center include comprehensive data evaluation efforts aimed at providing

high quality data for use in modeling/predicting processes in the upper atmosphere, especially those relevant to modeling stratospheric ozone layer perturbations. This work is supported by NASA and the EPA.

Important **energy-related** projects include the DoE-sponsored experimental project aimed at understanding solar energy storage mechanisms, and a data evaluation project concerned with the kinetics of combustion processes, also sponsored by DoE. The goal of this project is the production of a complete, self consistent evaluated data base of kinetic data for use in the modeling of hydrocarbon combustion. A related project, sponsored by the Joint Army-Navy-NASA-Air Force (JANNAF) Panel on Kinetic and Related Aspects of Propellant Chemistry, is concerned with the development of a similar database for propellant combustion. Dr. Wing Tsang, the principal investigator for both these projects, was invited during the year to provide expert testimony to a panel of the European Community Scientific Programme on Combustion about topics relevant to the evaluation of kinetic data for combustion.

In addition, during 1992, the Division's oxygen-bomb calorimetry laboratory certified two energy-related SRMs for use by the coal-fired power utility companies, the first (Heating Values of Coal) to monitor the properties of the coal used in their boilers, and the second (Benzoic Acid), to calibrate the bomb calorimeters used to determine the heating value of the coal used. The Benzoic Acid SRM is one of the five "best selling" SRMs produced at NIST. Also of interest to the power industries is the definitive work on the thermodynamic properties of aqueous sodium chloride solutions published this year.

Other Division research is oriented towards problems related to **industrial processes**. In an attempt to identify new avenues of research in this area, Dr. P.A.G. O'Hare was a co-organizer of a three-day symposium on "Thermodynamics in the Industrial Environment" which addressed topics such as the application of thermodynamics to reactions in thin films, advanced batteries, silane plasmas, the aluminum industry, and polymer glasses.

Current work in the Division includes the development of detection techniques for chemical vapor deposition in the Division's state-of-the-art resonance-enhanced multiphoton ionization (REMPI) laboratory, the exploration of the chemical mechanisms associated with chemical vapor deposition, the development of a database for dry etching and semiconductor manufacture, and unique calorimetric measurements relevant to advanced manufacturing. The latter effort was expanded this year by the construction of a new laboratory facility for low temperature adiabatic heat-capacity calorimetry. Two new projects were initiated during the year in support of an Advanced Technology Program-supported project concerned with metalorganic chemical vapor deposition (MOCVD). The projects involved the generation of a catalogue of evaluated data relevant to the fundamental gas phase reactions needed for models of MOCVD processes, and the experimental development of REMPI and laser induced fluorescence (LIF) detection schemes for free radicals involved in MOCVD.

Division involvement with **analytical chemistry**-related projects goes back many years. Kinetic research carried out in these laboratories in the 1960's laid the basis for the development of an analytical technique now called Chemical Ionization Mass Spectrometry; the early research program has evolved into a project now fully funded by DoE on mass spectrometric studies of the mechanisms and thermochemistry of chemical ionization processes.

The project in the Division which probably has the widest visibility outside of NIST is the maintenance and improvement of the NIST/EPA/NIH Mass Spectral Database, a large database of electron mass spectra which is in use in thousands of analytical chemistry laboratories throughout the world. The collection of spectra is distributed to the public as a searchable database for personal computers, and in a tape format. All the major manufacturers of analytical instrumentation are distributors of the tape version, which is made available to the public as an integral part of the data systems of commercial mass spectrometers. Work on this database, which originated several years ago at the EPA and was transferred to NIST four years ago, has become one of the Division's most vigorous programs, and has led to numerous spin-off activities. For example, software originally developed for the mass spectral database has been adapted for use with infrared spectra and for structural and sub-structural searching, and as a result, two new database products - a personal computer vapor phase infrared database and a product which predicts properties of molecules based on user-generated structural drawings - are now available from the SRDP. The program has resulted in a good example of direct government-industry technology transfer; Dr. Stephen E. Stein maintains active collaborations with programmers from most major instrument companies (such as Hewlett-Packard and Perkin Elmer) to aid in implementing software developed at NIST for the improvement of the reliability of library searching in commercial mass spectrometers.

Division scientists are in the forefront of work on the **development of software for use with personal computer-based chemical databases**. The professional quality of this software is such that Division scientists are in demand for collaboration on database-development projects originating outside the Division. For example, software for the database "NIST Spectroscopic Properties of Atoms and Atomic Ions" produced in the Physics Laboratory, was written by Dr. Gary Mallard; this database accounts for 10% of sales of personal-computer databases in the SRDP. Except for the mass spectral database, perhaps the best known computer-based database product generated in the Division is the Chemical Kinetics Database, which provides an output mechanism for the combustion and upper-atmosphere data evaluation projects; this database has sold more copies - nearly 900 - than any other single personal computer database distributed by the SRDP.

Another valuable by-product of Division data evaluation programs is the development of **estimation methods** to allow the prediction of data for species for which no experimental measurements are available. Work was continued this year on estimation of thermodynamic properties of organic liquids; a major collaborative effort in this area, to involve scientists from all over the United States, is being organized by SRDP to be spearheaded by work in this Division.

Division scientists are leaders in their professional fields. For example, Drs. P.A.G. O'Hare and John Herron serve as chairmen of the International Union of Pure and Applied Chemistry (IUPAC) Commissions on Thermodynamics and on Kinetics, respectively, while other Division members are secretaries of committees of those Commissions. Dr. O'Hare is the Editor-in-Chief of the Journal of Chemical Thermodynamics. Dr. R.E. Huie is the principal organizer of the Third International Conference on Chemical Kinetics, to be held at NIST in the summer of 1993. Division members are also active on committees of the American Society for Testing Materials (ASTM) and the International Council of Scientific Unions Committee on Data for Science and Technology (CODATA). Drs. R.F. Hampson and M.J. Kurylo are members of the NASA Panel for Data Evaluation which recommends definitive values of numeric data for modeling stratospheric chemistry. Dr. Kurylo is Acting Manager of NASA's Upper Atmosphere Research Program and Chairman of the Scientific Steering Committee of the International Network for the Detection of Stratospheric Change, with a wide range of scientific management and international scientific assessment responsibilities. This year, Dr. Kurylo also served as Program Manager/Scientist for NASA's Airborne Arctic Stratospheric Expedition II; this expedition sampled the upper atmosphere for experimental information about stratospheric ozone depletion.

Another evidence of the vitality of Division programs is the large numbers of citations gleaned by Division publications. For example, the data compilations published by Division Data Centers in books or journals were cited more than 1000 times in 1992.

In 1992, Dr. Stephen E. Stein received the Henry H. Storch Award in Fuel Chemistry sponsored by the American Chemical Society and Exxon Research and Engineering Company for distinguished contributions to fundamental or engineering research on the chemistry and utilization of coal.

**B. Selected Technical Reports
(Chemical Kinetics and Thermodynamics Division)**

1. Stability of Halocarbons in the Atmosphere

M.J. Kurylo, R.E. Huie, A. Fahr, E.P. Hunter, W. Braun, R.D. Saini (Bhaba Atomic Research Center, India), and Z. Zhang (Catholic Univ. of Leuven, Belgium)

This program, supported by NASA and EPA, focusses on the measurement of gas phase kinetic and photochemical parameters for important atmospheric constituents. The research emphasizes those processes that relate to our understanding of the fate of natural and anthropogenic trace gases in the troposphere and their chemical role in altering stratospheric composition. Major goals of this work include predicting the impact of human activities on stratospheric ozone and on global climate.

Recent laboratory accomplishments include flash photolysis-resonance fluorescence measurements of the rate constants for the reactions of hydroxyl radicals with compounds being developed by the chemical industry as possible replacement compounds for the chlorofluorocarbons (CFCs) commonly used as refrigerants. Hydroxyl radicals are the major reactive species in the troposphere which scavenge organic compounds released to the atmosphere. During the past year, technical papers were prepared describing the kinetics of the reaction between hydroxyl radicals and CH_3CFCl_2 (HCFC-141b, one of the most promising CFC replacement compounds), $\text{CH}_3\text{CF}_2\text{Cl}$ (HCFC-142b), and CH_2FCF_3 (HCFC-134a). This study has helped to clarify some of the uncertainties in the reactivities of these molecules at tropospheric and stratospheric temperatures.

Manuscripts have also been prepared on the atmospheric reactivities of several partially fluorinated ethers (one of which is under consideration as a replacement for the primary cooling fluid in the gaseous diffusion process used for uranium isotope enrichment in the United States), selected hydrofluorobutanes, and methyl bromide (which is widely used as a soil and commodity fumigant internationally). In some of these cases, it has been possible to develop a coarse reactivity scale that may be useful in estimating the atmospheric lifetimes for some of the molecules for which laboratory kinetic data do not exist.

Dr. M. J. Kurylo was invited in 1992 to participate in a Methyl Bromide Science Workshop and present the latest data from the NIST upper atmosphere kinetics laboratories; Dr. Kurylo was subsequently asked to serve as one of several authors for a report prepared for the Parties to the Montreal Protocol. This report constitutes an interim summary of the current understanding of the relationship of methyl bromide to the ozone layer. Dr. Kurylo also was one of four lead authors of a chapter entitled "Heterogeneous Processes: Laboratory and Field Studies" for an assessment entitled "Scientific Assessment of Ozone Depletion: 1991" prepared as part of the scientific review provisions of the Montreal Protocol.

A collaboration with researchers at the Ford Motor Company has resulted in the continuation of an investigation on the reactivity of the hydroxyl radical with potential fuel additives for internal combustion engines. Manuscripts prepared this year describe results for primary, secondary, and tertiary, and cyclic alcohols, as well as *tert*-amyl methyl ether.

Because the photolytic lifetime of a molecule in the upper troposphere and lower stratosphere depends on the absorption cross section in the far ultraviolet and ultraviolet, data on the absorption coefficients of the alternate halocarbons, both below and above the oxygen absorption cut-off, are needed. At the longer ultraviolet wavelengths (where the light flux is high and absorption can be important), the cross sections are so low that measurements are difficult and unreliable. Work in this laboratory has demonstrated that absorption coefficients measured in the liquid phase (where the high density permits the achievement of higher optical depths for a given path length than those attainable in the gas phase) can be reliably converted to the corresponding gas phase coefficients.

Use of this approach extends the wavelength range over which accurate absorption coefficient values can be determined. The method minimizes some of the systematic errors that accompany the measurement of extremely low gas phase absorptivity in the ultraviolet and can potentially be used over a wide range of temperature. Work this year focused on quantitatively analyzing the role of small levels of scattered light in the measurements, and provided an explanation for discrepancies in data appearing in the recent literature. New measurements will continue to focus on the room temperature absorptivity of several HCFCs in the spectral region from 250 nm to about 190 nm, with preparations being made for investigating temperature dependencies in the temperature range characteristic of the upper troposphere and lower stratosphere.

2. Kinetics Data Evaluation: The Upper Atmosphere Database

R.F. Hampson

The Chemical Kinetics Data Center provides the NASA Panel for Data Evaluation with evaluations for the chemical kinetics of atmospheric reactions involving halogenated species. Dr. Robert Hampson of the Data Center is a member of this panel, which this year published "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 10". Paralleling this activity, Dr. Hampson is also a member of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. For this organization, the Chemical Kinetics Data Center has the primary responsibility for evaluation of the chemical kinetic and photochemical data for reactions of halogenated species and selected oxygenated species. The IUPAC panel's "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Supplement IV" will be published this year in the Journal of Physical and Chemical Reference Data.

The Stratospheric Chemistry Database, which includes all the data evaluated for the two panels described above, gives a recommended rate constant value, along with a measure of its reliability and supporting documentation for each reaction. This year, evaluations were carried out on the kinetics of reactions of ClO_x , BrO_x and FO_x compounds.

A major publication of the World Meteorological Organization Global Ozone Research and Monitoring Project, "Scientific Assessment of Ozone Depletion: 1991" appeared this year. Dr. Robert Hampson was an editor of this publication.

3. Chemical Thermodynamics Data Evaluation: JANNAF Thermochemical Tables for Species of Importance to Ozone Depletion

D.B. Neumann

The objective of this project being carried out by Dr. D. B. Neumann of the Chemical Thermodynamics Data Center in collaboration with Malcolm W. Chase of the Standard Reference Data Program, is to provide the NASA Upper Atmosphere Program with a comprehensive evaluation of the thermodynamic data for stable as well as transient species involved in the network of reactions related to the destruction of ozone in the upper atmosphere.

Last year, evaluations were carried out on the following species:

OH , OH_2 , HCl , HOCl , HOClO , HOClO_2 , HOClO_3 , ClNO_2 , ClONO , ClONO_2 .

A manuscript on the evaluation of thermodynamic data for these chlorine cycle-related species is being prepared for publication in the Journal of Physical and Chemical Reference Data.

During 1992, work was initiated on the evaluation of data on analogous bromine-containing species:

HBr , HBrO , BrO , BrO_2 , HBrO_3 , HBrO_4 , BrNO_2 , BrONO .

Annotated bibliographies for the species have been assembled and the relevant data are being extracted. Due to various reaction networks, or pathways, experimental thermodynamic data for a number of the species are closely related to the thermodynamic properties of several of the molecules evaluated previously. Data summaries of the relevant thermodynamic and spectroscopic data are being written. Relevant quantum chemical calculations are being carried out as needed.

4. Combustion Chemistry

W. Tsang

This project has as its focus the development of a fundamental quantitative understanding of high temperature reactions of organic compounds so that large scale phenomena such as combustion can be fully described in terms of elementary thermal reactions. Experimental investigations are carried out in a unique heated single pulse shock tube. Selection of specific systems for study is largely guided by the affiliated data evaluation effort described below (see Chemical Kinetics Data Evaluation) with an emphasis on obtaining results which are needed to develop and validate correlation schemes for the prediction of rate expressions.

During the past year, a paper describing the kinetic properties of the allyl radical was prepared. Such resonance stabilized organic radicals play an important role in the chemistry of organic systems at high temperatures because their long thermal lifetimes enable them to survive to undergo a variety of reactions. Other collaborative work with scientists at Catholic University resulted in a paper on the decomposition of the ethyl radical.

Experimental studies on the decomposition of 1-octyne have been initiated. The aim of the work is to study the mechanism of the decomposition of 1-pentyl radical. Of particular interest is the possibility of radical isomerization prior to decomposition via beta C-C bond fission which apparently does occur, according to preliminary results. Rate expressions for this process will be determined. Although hydrocarbon decomposition kinetics are generally well understood, the problem of such rearrangements is an important remaining conceptual question in the field.

Experiments in liquid phase pyrolysis were initiated with the intention of developing a more fundamental understanding of the mechanism of dioxin formation during incineration processes. Initial studies of reactions in phenol and o-chlorophenol led to the identification of products formed at temperatures near 400 °C. Much progress has been made in the study of the liquid phase pyrolysis of chlorophenol. A serious experimental problem dealing with the stability of the sealed tubes has been solved. The conditions for the formation of the non-chlorinated dioxins have been defined. Results obtained in the presence of added CuCl₂ indicate that the reaction is catalyzed by the additive, with the initial reaction occurring at a temperature at least 100 °C lower than in the absence of the additive.

A chapter entitled "Dioxins and Furans" is being completed for a book entitled Handbook of Waste Incineration.

5. Chemical Kinetics Data Evaluation: Combustion and Propellant Databases

W. Tsang

A long range program, supported by the Department of Energy in the Chemical Kinetics Data Center, is directed at producing a complete database of self-consistent, evaluated kinetic data for use in the modeling of hydrocarbon combustion. The goal is an evaluated database covering all data pertinent to combustion of the C_1 - C_4 alkanes and methanol. A related effort sponsored by the JANNAF Panel for Propellant Combustion involves the evaluation of similar data for propellant combustion processes. The evaluation of thermal rate data important for combustion phenomena is closely tied to Dr. Tsang's program of experimental studies described above under the heading "Combustion Chemistry".

Earlier publications generated under the Combustion Chemistry project dealt with reactions involving methane, methanol, propane, n-propyl and isopropyl radicals, isobutane, t-butyl and isobutyl radicals, propene and allyl radicals. Over the past year, Part 5 on reactions of propene was published, and Part 6, which resolves a long standing problem in the interpretation of data on reactions involving 2-butene and 2-butenyl, has almost been completed. Work has begun on Part 7, on reactions of butadiene and butadienyl.

Part 2 of the Propellant Chemistry Data Base, which includes data pertinent to the reactions of CN, NCO and HNCO, was published in the Journal of Physical and Chemical Reference Data this year. Previously-published work had covered the reactions of NO, NO_2 , HNO, HNO_2 , HCN and H_2O ,

In related work, data on the stability of organic radicals are being evaluated in collaboration with Prof. D. Gutman of Catholic University. With Prof. J.H. Kiefer of the University of Illinois, a collaboration on the interpretation of the kinetics of unimolecular reactions studied over broad ranges of temperature is being initiated. Data concerned with SiO formation and destruction in silane flames are being evaluated in collaboration with Dr. M. Zachariah of the Process Measurements Division (836). With Dr. D. Burgess, also of Division 836, a computer simulation of the incineration of chlorinated organic compounds was carried out in 1992, and has been published.

6. Solar Energy Conversion and Storage

P. Neta, M. Kumar (Bhaba Atomic Research Center, India), J.P. Mittal (Bhaba Atomic Research Center, India), and D.M. Guldi (Univ. of Cologne, Germany)

Because metalloporphyrins have broad absorption spectra in the visible light range and also display rich redox chemistry, many of these compounds are efficient photosensitizers for solar energy conversion and storage. Experiments are designed to elucidate individual steps in reaction mechanisms pertinent to the conversion of solar energy into chemical energy.

Pulse radiolysis and laser flash photolysis techniques are used to study the kinetics and mechanisms of reactions important in the catalytic oxidation of water to oxygen and the reduction of water to hydrogen, utilizing metalloporphyrins as photosensitizers. Since reduction and oxidation of the metalloporphyrins themselves may take place on the ligand or on the metal center, and since only the latter are useful for catalysis, structural and medium effects on the path of electron transfer in several metalloporphyrins have been studied. Studies of several metalloporphyrins (Ni, Cr, Fe, Mn) reduced at the metal center and reactions with radicals that may lead to formation of metal-carbon bonds (leading to species that may play an important role in catalysis) are now in press. The possibility of reduction of CO₂ by a reduced metalloporphyrin and of insertion of CO₂ into a metal-carbon bond is now being explored. Studies are carried out with various cobalt complexes, porphyrins, cobalamine, and cobaloxime.

Another interesting and biologically important reaction in metalloporphyrins is the reversible migration of an alkyl group between the metal center and the pyrrolic nitrogen, which is induced by reduction or oxidation. The rate of reduction-induced methyl group migration was measured in N-methyl-Co(II)-porphyrin, and the identity of the product as CH₃-Co(III)-porphyrin was confirmed. The analogous reaction involving the N-methyl-Ni(II)-porphyrin, however, yields only Ni(II)-porphyrin upon reduction because the initial product contains an unstable Ni-C bond which undergoes homolysis. Further studies on Ni-C bonds in porphyrin complexes have been carried out and the results are now in press.

7. Aqueous Free Radical Kinetics

R.E. Huie, P. Neta, and S.A. Padmaja (Indian Institute of Technology)

This work includes studies of the reactions of inorganic radicals and of organic peroxy radicals in solution. The former are of interest because of their possible role in the environment and for industrial chemistry, while the latter studies have led to information which helps in understanding the biological activity of these radicals and assessing the potential toxicity of industrially important compounds.

The long-term project on the investigation of the kinetics and activation parameters for reactions of inorganic radicals continued in 1992. Results obtained were concerned with addition and electron transfer reactions of Cl_2^- , as well as the effects of solvents on activation energies. Studies on the rates of reaction of several inorganic radicals, including SO_4^- and NO_3^- in aqueous/organic mixtures, are being completed. The reactivities of the radicals SO_4^- and NO_3^- are affected differently by solvents, apparently because of specific solvation effects on reactants and transition states.

The new laser-flash photolysis facility employed for much of the above work was also used to carry out some photochemical studies. In the laser-flash photolysis of H_2S solutions, the spectrum and absorptivity of the $\cdot\text{SH}$ radical, the dimerization rate constant, the rate constant for reaction with O_2 and the rate constant for formation of the dimer radical anion, S_2H_4^- , were determined. Also, a study of the photochemistry of hydrazine, methyl- and dimethyl hydrazines has been carried out. Transient spectra were recorded and rate constants for the reactions of these transients with O_2 were determined.

Recent results impact on a reaction which is of considerable current interest in physiological chemistry, the reaction of nitric oxide, NO , with the superoxide anion, O_2^- . The results, soon to appear in Free Radical Research Communications, demonstrate that the reaction is very fast. Previous studies had concluded that the reaction was slow, so that there was some question about the importance of the nitric oxide reaction in biological systems. The NIST work showed that the reaction leads to the formation of the unstable species peroxyxynitrite ($^-\text{OONO}$) which decomposes to produce highly reactive free radicals. Such a reaction, in which the relatively unreactive O_2^- species generates a highly reactive product radical, may be of considerable physiological importance in the cell-killing activity of macrophages and neutrophils.

Solid particles are used as photocatalysts in a number of applications including solar energy conversion and waste-water treatment. A major goal this year was to initiate the study of the laser-flash photolysis of colloidal metal, metal oxide, and metal sulfide particles in the presence of selected substrates. This work has been started with an examination of TiO_2 particles.

8. Chemical Thermodynamics Data Evaluation: Aqueous Electrolytes

D.B. Neumann and D.G. Archer

Thermodynamic properties of aqueous electrolyte solutions have a wide range of applications from industrial process design to geology and biology. Two specific examples are the selection of corrosion control additives for boiler and turbine systems, and the modeling of geochemical processes involved in nuclear waste containment. The understanding, design, and prediction of chemical processes in such systems require knowledge of the equilibrium thermodynamics of aqueous solutions and/or the calculation of speciation in such solutions in heterogeneous phase equilibria. Accurate, reliable, and consistent thermodynamic data, including Gibbs energies

and/or equilibrium constants, activity and osmotic coefficients, and heat capacities, are required. The results of equilibrium calculations for aqueous systems can only be as good as the thermodynamic data available, and results of equilibrium calculations may be highly sensitive to the values of thermodynamic data used.

In 1992, the Aqueous Electrolyte Data Center was combined with the Chemical Thermodynamics Data Center, and the effort on evaluating data on the thermodynamics of aqueous electrolyte solutions was reduced, largely because Division scientists with expertise in this area were devoting attention to developing new projects.

Two papers on the thermodynamic properties of the (NaCl+H₂O) system by Dr. D.G. Archer were published this year in the Journal of Physical and Chemical Reference Data. The work includes new equations and/or values for $\Delta_f G_m^\circ$ and $\Delta_f H_m^\circ$ for formation from the elements for NaCl(cr) and NaCl·2H₂O(cr) (298.15 K and 0.1 MPa), and the change in chemical potential for both NaCl and H₂O in NaCl(aq) as a function of temperature, pressure, and molality, valid from 250 to 600 K and, where available, from the vapor pressure of the solution to 100 MPa. Work on one of these manuscripts carried out this year included an examination of unusual behavior of compressibility functions and the determination of an additional set of parameters for the equation of state. The second set of parameters were consistent with the use of a different dielectric-constant equation. A program that calculated thermodynamic properties for NaCl(aq) was prepared for general distribution.

9. Precision Oxygen Bomb Calorimetry: Calorimetric Reference Standards and Thermodynamic Properties of Organic Phosphorus and Strained Organic Compounds

D.R. Kirklin

Precision bomb calorimetry provides the data necessary to calculate precise and accurate enthalpies of formation which are necessary to evaluate the molecular energetics of important materials and the thermodynamic feasibility of their chemical reactions. The NIST oxygen bomb calorimetry laboratory has unique, well-characterized calorimetry equipment which is capable of making combustion measurements on samples as small as 10-15 milligrams. The capability of handling such small samples permits routine measurements on substances which are available only in small quantities, such as very high purity compounds. The laboratory also has the capability of carrying out bomb calorimetric measurements in either a static or a rotating mode. Accurate calorimetric results on organic compounds that contain sulfur, phosphorus, or halogens can be obtained only through use of a rotating bomb calorimeter.

Because of these unique facilities, the NIST oxygen bomb calorimetry laboratory is the only laboratory that is presently making precise and accurate measurements on organic phosphorus and strained organic compounds. Many of the novel materials of interest today are only available

in extremely limited quantities. For example, last year, the laboratory carried out the first reported results on the thermodynamic properties of C₆₀ fullerene, working with a 99% pure sample. This year, a high purity sample of this unique compound was acquired from Drexel University, and a complete study was made of its thermodynamic properties.

Because of the complete lack of thermodynamic data on organic compounds containing both phosphorus and sulfur, work was undertaken this year to determine heats of combustion of such compounds. These data are needed to develop a reliable estimation scheme for predicting the thermodynamic properties of organic phosphorus compounds not amenable to experimental measurements because of their hazardous properties. The U. S. Army, in particular, needs such data in order to design methods for the destruction of chemical agents. This project required extensive work on sample preparation and characterization, including quantifying the heat of mixing of phosphoric acid-sulfuric acid mixtures and designing a method to purify a sample of triphenyl phosphine sulfide for meaningful combustion calorimetric measurements. The recently completed study is being prepared for publication.

In addition to the measurements on novel compounds of special interest, determinations of thermodynamic properties are also made on materials which are available in large quantities. The most important projects in this class in 1992 were the certification of a new batch of the NIST calorimetric Standard Reference Material (NIST SRM 39i), benzoic acid, and the certification of two Standard Reference Materials on the Heating Value of Coal.

10. Fluorine Bomb Calorimetry: Thermodynamic Properties of Materials Important in Modern Technologies

P.A.G. O'Hare

A key thermodynamic property of all substances is the standard molar enthalpy of formation. In the past this quantity has been determined experimentally by such techniques as solution calorimetry in aqueous media or combustion calorimetry in high-pressure oxygen (as in the Division's Oxygen Bomb Calorimetry laboratory). In general the properties of "high-tech" materials can not be determined by such procedures; however, the exceptional oxidizing power of high-pressure fluorine can be brought to bear using the technique of fluorine-combustion calorimetry, thus permitting the experimental determination of the enthalpies of formation of such substances. The NIST fluorine bomb calorimetry laboratory is the only one of its kind in the world.

The objective of the fluorine bomb calorimetry laboratory is to establish, primarily by experimental methods, a database of key thermodynamic information for pure materials of importance in modern technologies. For example, during the past year a collaborative effort headed by NIST and involving researchers in Australia, Canada, and the Netherlands succeeded

in elucidating the thermodynamic behavior of tungsten ditelluride (WTe_2), which is used as a high-temperature lubricant and in photovoltaic cells.

Amorphous (glassy) forms of the chalcogenides of Groups IVB and VB of the periodic table are used in many switching and memory devices. Thermodynamic studies of these materials are necessary in order to understand their thermal stability and chemical bonding, optimal methods of synthesis, vapor deposition, interactions with substrates, and the fabrication of optical fibers. (Germanium + sulfur) is such a system recently studied in the NIST laboratory. The results show that the energy difference between the crystalline and vitreous forms of GeS_2 and of GeSe_2 are almost the same, which suggests that, surprisingly, the long-range intramolecular forces are of comparable magnitude in both compounds.

Thermodynamic investigations of materials used in silicon integrated circuits are necessary in order to understand the chemistry of the basic metal silicides, their interactions with interconnects composed of other metals, and the chemical mechanisms of "dry etching". One of those substances, tungsten disilicide (WSi_2), has now been studied in detail, yielding information which permits a prediction of how WSi_2 will behave under the various scenarios mentioned. The conclusions of this study were presented at a recent SEMATECH/NIST workshop.

Recent results on the semiconductor silicon sesquitelluride, Si_2Te_3 , whose primary technological use is as an optical recording material, will help elucidate its behavior at the high temperatures to which it is exposed in manufacturing processes.

Future work will focus on vitreous materials in order to further our rather limited understanding of chemical bonding in the amorphous state. In collaboration with scientists at Argonne National Laboratory, an attempt will be made to prepare crystalline and vitreous SiS_2 .

11. Low Temperature Heat Capacity Calorimetry: Thermodynamic Properties of Materials Important in Modern Technologies

D.G. Archer

This year, work was initiated to set up a low temperature heat capacity calorimetry laboratory to broaden the Division's capabilities to provide useful thermodynamic information to the user communities. This new facility, along with the existing bomb calorimetry laboratories, will give the NIST thermodynamics laboratories the capacity to carry out the full range of measurements necessary to predict chemical equilibrium constants for systems of interest.

The equilibrium constant of a chemical reaction tells us what the extent of reaction is, that is, how much product and reactant exist at equilibrium. Examples of large-scale industrial processes built on knowledge of particular equilibrium constants are: fossil-fuel refining, large-scale amino acid production, corrosion, and inorganic chemical production. The equilibrium constant is

simply related to the thermochemistry of the reaction, and can be obtained if values of the enthalpy change and entropy change of the reaction are known. These quantities can, in turn, be derived from standard enthalpies and entropies of formation of the relevant chemical compounds taking place in the reaction.

Values of entropies are usually obtained from an integration of heat capacity data over a wide range of temperature. Since Division bomb calorimetry laboratories generate data on enthalpies of formation, after completion of the new facility, the NIST thermodynamics laboratories will possess the ability to determine absolute values of all parameters necessary to predict chemical equilibrium constants, and will be one of only two laboratories in this hemisphere with this capacity. Two low-temperature adiabatic calorimeters will be ready for operation in the near future.

The new laboratory will operate in collaboration with the Division's bomb calorimetry laboratories on projects directed toward determination of the heat capacities, that is the entropies, of industrially and technologically important materials. The materials that are candidates for investigation in this new program come from three broad fields. These are: (1) Materials important to the inorganic-materials sciences, including among others, structural refractory materials and materials used in solid-state electronics device construction with a focus on determining the thermodynamic stability of these materials in the harsh operating environments to which they are often exposed. (2) Chemical process effluent waste treatment. This relates to the increasing needs of industry to process and recycle effluent streams from their chemical reactors. (3) Substances for which thermodynamic data are required in order to give scientists a consistent set of data on underlying and important thermodynamic properties.

12. Optical Studies of Reactive Intermediates

J.W. Hudgens, R.D. Johnson III, K.K. Irikura, and J.L. Brum

Resonance enhanced multiphoton ionization (REMPI) spectroscopy provides previously unobtainable data about the electronic structures of a wide variety of free radicals. Newly discovered REMPI spectra form the basis of new sensitive and selective schemes for the optical detection of these radicals. The technique involves tuning an intense pulsed dye laser so that the energy sum of two or three photons of laser light matches the energy of a Rydberg state of the radical of interest. Laser-excited radicals in Rydberg states then absorb an additional photon and ionize. The ionization signal is measured by detecting ions with mass spectrometry or by detecting the laser-induced electron current. REMPI detection schemes are very selective and typically give sensitivities between 10^4 - 10^{10} radicals cm^{-3} .

A particularly important result achieved this year was the publication of the first simple, conveniently applied detection schemes for ground state methylene radicals, CH_2 ($\tilde{X}^3\text{B}_1$). Because CH_2 plays extremely important roles in combustion and photochemistry of hydrocarbons,

researchers have long wanted a sensitive optical diagnostic method. Two new REMPI schemes were reported. One scheme uses a pulsed dye laser tuned near 400 nm which excites three-photon resonances with the previously known 3d and 4d Rydberg states. The second scheme uses ~312 nm laser light to excite two-photon resonances with the 3p and 4p Rydberg states - states that were also discovered this year in the REMPI laboratory. Both detection schemes achieve sensitivities better than 10^7 radicals-cm⁻³. During the next year, these new detection schemes will be applied to the observation of an air-methane flame, and also will be used to study a filament pyrolysis source similar to one used in a diamond chemical vapor deposition (CVD) reactor.

Recent work in the REMPI laboratory continues to emphasize the development of nonintrusive, laser-based detection methods for radicals important to semiconductor materials. This year, extensive studies on the SiCl₃ and CHF₂ radicals which relate to silicon CVD and reactive etching were published. The data contained in these papers will also improve future thermochemical determinations of SiCl₃ and CHF₂ radicals and ions. In addition, results of a study of the NH radical were published. New REMPI detection schemes were also obtained for boron radicals including B, BH, BF, BF₂, BCl, and B₂. Such radicals are proposed to be present in CVD reactors that are depositing P- and N-doped diamond films.

In connection with the studies of SiCl₃ and CHF₂ radicals, GAUSSIAN 90 *ab initio* calculations were carried out to help interpret REMPI vibrational spectra and to refine thermochemical values. Our calculational efforts will increase when we acquire advanced programs based upon density functional theory (e.g., DMol) to help design and interpret experiments to study transition metal systems. For example, we expect such calculations to help with our recently initiated experiments designed to discover spectra of the radical precursors of titanium silicide films. Such films are used in very large-scale integrated circuits.

13. Kinetics Data Evaluation: The Plasma Chemistry Database/Data Relevant to CVD

J.T. Herron

The Chemical Kinetics Data Center is collaborating with the Electrosystems Division of NIST through a CRADA "Investigation of the Production of S₂F₁₀ in Compressed SF₆-Insulated Power Equipment", involving EPRI and a group of electric utility companies in providing data on the chemistry of dielectric breakdown of SF₆. This year, Dr. John Herron developed a model to explain the formation of S₂F₁₀ (previously predicted and now detected), SF₅OSF₅, SF₅OOSF₅, SF₅OF and higher analogues as breakdown products of SF₆. An explanation was provided for the presence of S₂F₁₀ in the commercial manufacture of SF₆. Other on-going work involves a re-examination of shock tube data on SF-compounds, with a study of the unimolecular decomposition of SF₄.

A new project initiated during the year, in support of an Advanced Technology Program-supported project concerned with metalorganic chemical vapor deposition (MOCVD), involved the generation of a catalogue of evaluated data relevant to the fundamental gas phase reactions needed for models of MOCVD processes. A database of physico-chemical data for silicon and germanium compounds has been compiled, and an annotated bibliography is being prepared.

14. Kinetic Mass Spectrometry

L.W. Sieck

This program of research in ion/molecule reaction chemistry, supported by the Department of Energy, is directed at the determination and evaluation of ionic reaction mechanisms incorporating competitive reaction kinetics which may prove useful for analytical purposes. The analytical technique known as "chemical ionization mass spectrometry" is based on the chemical reactions of ions, generated in a mass spectrometer, with "unknown" substrate molecules; reactions of interest include proton transfer, hydride transfer, and electron transfer. Work in Division laboratories involves measurements of ion/molecule rate constants, and equilibrium constants of ion/molecule reactions as a function of temperature. The latter quantities lead to quantitative data on the acidities and basicities of isolated (e.g., gas phase) molecules, relative scales of ionization energies, and data on the thermochemistry of ionic clustering reactions. The latter information has many uses, including understanding nucleation events and the prediction of biological reactions.

In 1992, experimentally-derived thermochemical networks for clustering and ligand switching reactions were combined with results from beam expansion studies at Virginia Commonwealth University to provide a more detailed understanding of the various factors influencing cluster nucleation, growth, and stabilities. Several papers describing this work have been submitted for publication.

15. Ion Energetics Database

P.J. Ausloos, S.E. Stein, R.D. Levin, S.G. Lias, and P.C. Christian

The Ion Kinetics and Energetics Data Center produces collections and evaluations of data concerned with the kinetics and thermochemistry of ions in the gas phase, data of use for many applications of mass spectrometry and for modeling certain plasmas, the ionosphere, systems under high energy irradiation, etc. The Data Center maintains collections of data on ionization energies of molecules, appearance energies of fragment ions, proton- and electron-affinities, and the thermochemistry of ionic clusters. Data Center publications are widely cited, collecting 520 citations in 1991, the last full year for which citation data are available.

A long-range goal of the Data Center has been to complete the task of putting together a complete collection of ionization energy and appearance energy data in a computer database archive, including values from measurements made before 1971, which have never been entered into computer files, and to provide the user community with a high quality automated version of that complete collection, which would include (a) all experimental measurements plus selected evaluations, (b) molecular structures, names and synonyms, and Chemical Abstracts Registry Numbers of all species, (c) enthalpies of formation of as many species (both ions and neutral precursors) as possible, (d) search modes by formula, name, Registry Number, or by data values.

During 1992, significant progress was made toward those goals. The entry of data which appeared in the time span 1971-1991 was completed. Because there are no existing computer files for Data Center publications containing pre-1971 data, a scanner is being used to enter the contents of those books into a computer file, which is being carefully proofread and edited. The data from the older collection will require the acquisition of Chemical Abstracts Registry Numbers for all compounds not already included in the data collection, and the entry of structural data on the molecules into the computer file.

An update of the personal-computer version of the database is being generated using the software called "Structures and Properties" (described under "Chemical Database Development" below). For this product, structural drawings have been produced for all 15,000 compounds included in the collection, and Registry Numbers and numerous chemical names and synonyms for all 15,000 compounds are part of the database.

Data on the energetics of ionic clusters have been entered into a database, and are now being evaluated in collaboration with Dr. Michael Mautner. A computer database and a publication in the Journal of Physical and Chemical Reference Data will result.

16. Chemical Thermodynamics Data Evaluation: Heat Capacities and Entropies of Organic Compounds, Estimation of Thermodynamic Properties of Organic Compounds

E.S. Domalski and V. Ruzicka (Institute of Chemical Technology, Czechoslovakia)

Much of the current emphasis of work in the Chemical Thermodynamics Data Center is on the evaluation of thermodynamic data for organic compounds, with the long-range goal of developing a definitive scheme for estimating thermochemical data. Such expert schemes permit the user community to readily estimate needed information for the thousands of organic compounds for which no experimental measurements have ever been made.

The second-order group-additivity estimation method, which has been applied so successfully by S. W. Benson and co-workers to the estimation of thermodynamic properties ($\Delta_f H^\circ$, C_p° , S°) of gas phase molecules, has been extended to the condensed phase for organic compounds

containing carbon, hydrogen, oxygen, nitrogen, sulfur, and halogen atoms; the analysis upon which the estimation parameters were based included data for 1513 molecules. A 1190-page manuscript with over 1000 references, "Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K," is now being modified in response to reviewers' comments, and will be published in the Journal of Physical and Chemical Reference Data.

Other projects involve the compilation and estimation of heat capacities of organic liquids. A major publication, the IUPAC-sponsored compilation, "Heat Capacities of Liquids, Evaluated Data and Recommended Values" by M. Zabransky and V. Ruzicka (Institute of Chemical Technology, Prague), V. Majer (Universite Blaise Pascal/CNRS, France), and E.S. Domalski (NIST), has been approved for publication by the IUPAC Subcommittee on Thermodynamic Data and the IUPAC Commission on Thermodynamics. Dr. Ruzicka recently completed an 18-month stay at NIST as a Guest Researcher, during which time four publications were completed dealing with the estimation of the heat capacities of organic liquids as a function of temperature. A related project, the compilation entitled "Heat capacities and entropies of organic compounds in the condensed phase, Volume III" by E.S. Domalski and E.D. Hearing is near completion. The work, with nearly 2000 references, includes all data from the 1984 and 1990 publications of the same title, along with the data from 1990, 1991, and 1992. The work also includes thermodynamic data for phase transitions for solid/solid, solid/liquid, and in some instances, solid/gas and liquid/gas.

A bibliography and file of papers has been compiled which contains over 1200 references to data on the thermodynamic properties of organometallic compounds. Additional references are being collected for entry. This bibliography will serve as the basis for 1993 projects on the evaluation and estimation of the enthalpies of formation of organometallic compounds at 298.15 K.

Two personal computer-based databases, "THERM/EST" and "HEAT CAPACITY," based on these publications, are in preparation.

17. Data Compilation: Enthalpies of Formation of Organic Compounds

S.E. Stein and H.Y. Afeefy (Mansoura Univ., Egypt)

At the present time, there is no comprehensive collection of data on the enthalpies of formation of organic compounds available in a personal computer format. The standard books, Stull, Westrum and Sinke (1969), Cox and Pilcher (1970), Pedley and Rylance (1977), and Pedley, Naylor, and Kirby (1986) are out-of-date and some of them are significantly incomplete. Nevertheless, the need for such a compilation is easy to see when one realizes that these four publications collectively accrue many hundreds of citations each year.

During the past year, the effort aimed at providing a comprehensive collection of data on enthalpies of formation of organic compounds for use with the "Structures and Properties"

software (described under "Chemical Database Development" below) has been significantly advanced. Initially all the references included in the above-cited hard copy publications were retrieved and the data were abstracted. Subsequently all the data not included in those publications was located, and is now being abstracted; it is estimated that nearly 50% of the data available in the literature was missed in the previous compilations.

The plan is to quickly collect as much as possible of the existing relevant literature, and enter the data into a computer database. This database will be made available as a searchable product for personal computers, and as a hard copy publication. Data for organometallic compounds collected under a related Thermodynamics Data Center project (described above) will be included in this compilation.

The on-going collection of data on organic thermochemistry will eventually serve as the basis for the development of a definitive set of group additivity values for implementation of Benson's Group Additivity method of estimating thermochemical data, as described above under a description of on-going work in the Chemical Thermodynamics Data Center. This work will be carried out in collaboration with various scientists from other organizations, including Dr. Sidney Benson, the scientist who originally recognized the power of this approach and successfully implemented such schemes.

18. Chemical Database Development

**S.E. Stein, W.G. Mallard, A.A. Levitsky (Institute of Organic Chemistry, Russia),
and S. Kirchansky (Institute of Organic Chemistry, Russia)**

The Division has an active program for the development of software for use with the many chemical databases generated in Division Data Centers and, on occasion, with databases from other NIST Data Centers.

The primary output mechanism for data collected for the three Kinetics Data Center projects described above (Combustion, Upper Atmosphere, and Plasma Chemistry) is the personal-computer database package called the "NIST Chemical Kinetics Database," which is the most popular personal-computer database distributed by NIST, with nearly 900 copies sold. This package, designed and maintained by W. G. Mallard, provides a tool for rapidly retrieving kinetic data on a particular reaction, reactions of a given species, or all the data reported in a given literature reference. The software permits a graphic display of the temperature dependences of reaction rate constants, and allows a user to evaluate the data. Version 4.0 of the NIST Chemical Kinetics Database, released in 1992, contains over 16,800 records relating to over 7400 reactions (5800 reactant pairs). Data relating to electronically excited species were added for the first time. In addition, the database programs were modified to allow for searching based on reaction products.

A year ago, software designed by S. E. Stein known as "Structures and Properties" was first released for distribution. The software, a spin-off of programs originally developed for handling structural data used with the mass spectral database, includes structural and sub-structural searching for data associated with species drawn on the screen by the user, and generates estimated values of molecular properties (heats of formation, vapor pressures, boiling points) for molecules drawn on the screen by the user. A long-range goal is to put together large databases of experimental "structure and property" data to be used with this software. These will include all the databases developed in Division Data Centers which are relevant, including the database of ionization energies (implemented this year as described under "Ion Energetics Database" above), an existing collection of 16,000 vapor pressures and boiling points collected for use with the mass spectral database, a large collection of molecular structures, names, and Registry Numbers put together for Division databases, as well as heat capacities, retention indices, etc. An important spin-off project, the collection of data on enthalpies of formation of organic compounds is described separately.

Several databases from other NIST Data Centers were provided with software prepared in this Division during 1992. These include "The NIST Database of Spectroscopic Properties of Atoms and Atomic Ions" (containing data originally reported in NSRDS-NBS 68 and subsequent corrections), which was released this year. A collaborative project with the Notre Dame Radiation Chemistry Data Center on solution kinetics data will be released soon. Dr. Mallard is also preparing a database of spectroscopic properties of diatomic molecules, an update of the book "Spectroscopy of Diatomic Molecules" by Huber and Herzberg.

19. The NIST/EPA/NIH Mass Spectral Database

S.E. Stein, P.J. Ausloos, C.L. Clifton, S.G. Lias, A.A. Levitsky (Institute of Organic Chemistry, Russia), and S. Kirchansky (Institute of Organic Chemistry, Russia)

This large database of electron mass spectra is one of the most widely-known products of NIST, in use in thousands of commercial mass spectrometers. The collection was originally put together at EPA and NIH, and starting in 1978, was distributed by Standard Reference Data program while still being maintained by the EPA. In 1987, a fully searchable personal computer version of the database was developed at NIST by Dr. S. E. Stein, an accomplishment which resulted in the establishment of a Mass Spectrometry Data Center at NIST in 1988, with the mission of maintaining, updating, and improving the Mass Spectral Database.

The database is distributed in a personal computer version and on tape; the tape format is used almost exclusively by commercial enterprises, mainly manufacturers of mass spectrometers, who have an agreement with NIST under which they incorporate the database into the data systems of the instruments they sell. The database is used for so-called "library searching"; that is spectra of unknown compounds are compared to the spectra in the collection in order to locate similar spectra which will provide clues to the identity of the unknown sample. Data Center

activities focus on improving the quality and enlarging the size of the mass spectral database, and on the development of improved software for searching, matching unknown spectra, and locating/correcting errors. In addition, attention is given to developing auxiliary databases of use to analytical chemists.

In May, 1992, a new update of the mass spectral database was released. The update contains 62,500 spectra (8,200 of them new), as well as an auxiliary file of 12,500 fully evaluated replicate spectra. The new spectra include original spectra determined in Division laboratories and at NIH, and spectra donated by database users. In the 1992 release, for the first time structural data for all compounds in the database are included.

During the years when the database was maintained at EPA, the spectra were evaluated exclusively through use of a computer algorithm called the "Quality Index". After the maintenance of the database was moved to NIST, it became obvious that the Quality Index algorithm was simply not capable of detecting many common problems which occur in mass spectra; the long history of maintenance without human intervention had resulted in a database which contained a large number of errors. During the preparation of the 1992 update, Dr. P. Ausloos individually examined a large fraction of the spectra in the collection, making modifications, where necessary. The spectral evaluation work is continuing.

On-going activities aimed at enlarging the database will continue until the database contains all compounds which would be expected to be of interest for mass spectrometric analysis, such as spectra of industrially-important chemicals, chemicals appearing on EPA lists of environmentally important compounds, pharmaceuticals, pesticides, etc.

Some of the new spectra for the mass spectral collection are determined in Division laboratories using an instrument which simultaneously provides an infrared (IR) spectrum. These IR data were combined with an older public domain (EPA) vapor phase IR database, to generate a new database product, the "NIST/EPA Vapor Phase Infrared Database," which was released this year. The software used for the personal computer-based database is a modification of that developed for the PC version of the mass spectral database.

Other on-going work is focused on improving the software used for matching spectra of unknown compounds against mass spectral databases. Several instrument manufacturers have expressed an interest in using NIST-developed software in the data systems of instruments, and are working with Dr. Stein to implement this.

20. Planetary Atmospheres

A. Fahr

This project, supported by NASA, explores the reaction kinetics of radicals thought to play a role in carbon-rich atmospheres. Recent work has focused on the chemistry of the vinyl radical. Initial efforts this year were directed towards finding a convenient and clean source of vinyl radicals. From studies of the photodissociation of methyl vinyl ketone at 193 nm, it was determined that vinyl radicals are formed with a quantum yield close to unity. Various rate constants for vinyl and methyl radical reactions were determined through detailed kinetic modeling of the system. A paper describing the results has been submitted for publication.

A detailed error analysis for rate determinations in complex kinetic systems such as those studied in this project is in progress. In such systems, where several processes, absorptions, and species concentrations are involved, an analytic relationship involving concentrations and rate constants is often impossible to attain and numerical integration and modeling is required. In such determinations, systematic errors introduced by employing "imperfect" values for the parameters used in the modeling should be addressed and evaluated. Two papers describing kinetic modeling programs and error analysis for such systems are in preparation.

A new temperature-controlled cell for flash photolysis was designed, built and installed during 1992, and will soon be operational.

**C. Outputs and Interactions
(Chemical Kinetics and Thermodynamics Division)**

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2. Talks

Domalski, E.S., "Calorimetric Methods and Estimation Procedures for Crystalline Organic Compounds Containing Nitrogen and/or Phosphorus," Aberdeen Proving Ground, MD, July 17, 1992. Invited

Domalski, E.S., "Estimation of the Thermodynamic Properties of Solid Amino Acids and Peptides," 12th IUPAC Conference on Chemical Thermodynamics Joint Meeting with the 47th Calorimetry Conference, Snowbird, UT, August 18, 1992.

Hampson, R.F., "A Review of Kinetics Data for Bromine Reactions," Methyl Bromide Science Workshop, Arlington, VA, June 3, 1992.

Herron, J.T., "The Thermodynamics and Kinetics of SF_5 ," 12th International Symposium on Gas Kinetics, Reading, England, July 21, 1992.

Herron, J.T., "Chemical Kinetic Data for Modeling Non-Thermal Plasmas," Workshop on Non-Thermal Plasma Techniques for Pollution Control, Cambridge, England, September 22, 1992. Invited

Hudgens, J.W., "Studies of Polyatomic Free Radicals Using Resonance Enhanced Multiphoton Ionization Spectroscopy," University of Puerto Rico, November 28, 1991. Invited

Hudgens, J.W., "Multiphoton Ionization Spectra of the SiH_3 Radicals," 3rd Topical Meeting on Laser Applications to Chemical Analysis, Salt Lake City, UT, January 28, 1992. Invited

Huie, R.E., "The Gamma-Radiolysis of Sulfite Solutions," CHEMRAWN VII, Baltimore, MD, December 4, 1991.

Huie, R.E., "Laser-Flash Photolysis of H_2S Solutions," XXth Informal Conference on Photochemistry, Atlanta, GA, April 29, 1992.

- Huie, R.E., "Reaction of NO with O_2^- ," 5th Annual Dinner Meeting of the Oxygen Club of Greater Washington, Bethesda, MD, May 9, 1992.
- Huie, R.E., "Solvent and Temperature Dependence of the Rate Constants of Some Reactions of Inorganic Radicals," Gordon Research Conference on Radiation Chemistry, Newport, RI, July 9, 1992.
- Huie, R.E., "Rate Constants for the Reactions of O_2^- and $HO_2\cdot$ with HSO_3^- , SO_3^{2-} , and SO_5^- ," Symposium on Chemistry of the Atmosphere, 204th ACS National Meeting, Washington, DC, August 28, 1992. Invited
- Irikura, K.K., "Detection of CH_2 (X^3B_1) Radicals by 3+1 REMPI and by 2+1 REMPI," XXth Informal Conference on Photochemistry, Atlanta, GA, April 27, 1992.
- Irikura, K.K., "The 2+1 REMPI spectrum of $SiCl_3$," XXth Informal Conference on Photochemistry, Atlanta, GA, April 28, 1992.
- Irikura, K.K., "Electronic Spectrum of the $SiCl_3$ Radical," Ohio State University International Symposium on Molecular Spectroscopy, Columbus, OH, June 18, 1992.
- Irikura, K. K., "Resonance-Enhanced Multiphoton Ionization Spectroscopy of $CH_2(X^3B_1)$," Ohio State University International Symposium on Molecular Spectroscopy," Columbus, OH, June 18, 1992.
- Irikura, K.K., "Experiment and Theory: Vive la Difference!" Gaithersburg, MD, August 7, 1992. Invited
- Johnson III, R.D., " CH_2Cl Observed by REMPI Spectroscopy," Ohio State University International Symposium on Molecular Spectroscopy, Columbus, OH, June 18, 1992.
- Johnson III, R.D., "Rydberg States of CCl Observed by REMPI," Ohio State University International Symposium on Molecular Spectroscopy, Columbus, OH, June 18, 1992.
- Kurylo, M.J., "The Atmospheric Lifetime of Methyl Bromide," Briefing and Informal Workshop Held by Senator Albert Gore on the Ozone-Depleting Effects of Methyl Bromide, Washington, DC., February 1992. Invited
- Kurylo, M.J., "Stratospheric Ozone Science: Past, Present, and Future," Keynote Address at the Annual Meeting of the Air Conditioning and Refrigeration Institute, Palm Springs, CA, November 1991. Invited
- Kurylo, M.J., "Interim Results from the Second Airborne Arctic Stratospheric Expedition," NASA Press Conference, Washington, DC, February 1992. Invited

- Kurylo, M.J., "The Network for the Detection of Stratospheric Change," UV-B Monitoring Workshop sponsored by Chemical Industry and the USDA, Washington, DC, March 1992. Invited
- Kurylo, M.J., "Latest Advances in Our Understanding of Stratospheric Ozone," Keynote Address at the City of Toronto Earth Day Festivities, Toronto, Canada, April 1992. Invited
- Kurylo, M.J., "Important Scientific Milestones in the Study of Stratospheric Ozone," Canadian Atmospheric Environment Service Laboratory Seminar, Downsview, Canada, April 1992. Invited
- Kurylo, M.J., "Preliminary End-of-Mission Results from the Second Airborne Arctic Stratospheric Expedition," NASA Press Conference, Washington, DC April 1992. Invited
- Kurylo, M.J., "Scientific Highlights from the Second Airborne Arctic Stratospheric Expedition," Alternate Fluorocarbons Environmental Acceptability Study (AFEAS) Science Committee Meeting, Ogunquit, ME, May 1992. Invited
- Kurylo, M.J., "A Review of the Conclusions of the Scientific Assessment of Ozone Depletion: 1992," Joint Session of the Scientific Steering Committee of Chemical Industry's Alternate Fluorocarbons Environmental Acceptability Study (AFEAS), Ogunquit, ME, May 1992. Invited
- Kurylo, M.J., "New Kinetic Measurements for the Reaction of Hydroxyl Radicals with Methyl Bromide," Methyl Bromide Global Coalition Scientific Workshop, Arlington, VA, June 1992. Invited
- Kurylo, M.J., "Recent Results from the Second Airborne Arctic Stratospheric Expedition (AASE II)," Quadrennial Ozone Symposium, Charlottesville, VA, June 1992. Invited
- Kurylo, M.J., "An Understanding of Northern Hemisphere Stratospheric Ozone Loss: Preliminary Data from AASE II," Upper Atmosphere Research Satellite Science Team Meeting, Aix-en-Provence, France, June 1992. Invited
- Kurylo, M.J., "Plans for a 1994 Airborne Southern Hemisphere Ozone Mission," Upper Atmosphere Research Satellite Science Team Meeting, Aix-en-Provence, France, June 1992. Invited
- Lias, S.G., "On the Ionization Energies of CCl_3 and CF_3 Radicals," 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, DC, June 1, 1992.

- Lias, S.G., "The NIST/EPA/NIH Mass Spectral Database: Recent Advances," NIST/EPA/NIH Mass Spectral Database Steering Committee, New Orleans, LA, March 10, 1992. Invited
- Lias, S.G., "What Will You Find in the New Version of the NIST/EPA/NIH Mass Spectral Database?" 40th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Washington, DC, June 3, 1992.
- Lias, S.G., "The NIST/EPA/NIH Mass Spectral Database: Recent Advances," Environmental Protection Agency Tentatively-Identified Compounds Committee, Alexandria, VA, July 16, 1992. Invited
- Mallard, W.G., "Evaluated Databases for Chemical Kinetics of Chemical Vapor Deposition," Sematech/NIST Workshop on CVD Processing in Semiconductor Manufacturing, Gaithersburg, MD, September 29, 1992. Invited
- Neta, P., "Reduction of N-methyl-Porphyrins of Co(II), Ni(II), and Cu(II). Redox Induced Methyl Group Migration." Sixteenth DOE Solar Photochemistry Research Conference, Delavan, WI, June 2, 1992.
- Neta, P., "Pulse Radiolysis Studies of Metalloporphyrins," Institute of Nuclear Chemistry and Technology, Warsaw, Poland, August 14, 1992. Invited
- O'Hare, P.A.G., "Fluorine as Oxidant in Combustion Calorimetry," Royal Military College of Canada, Kingston, Ontario, Canada, April 3, 1992. Invited
- O'Hare, P.A.G., "Recent Fluorine-Bomb-Calorimetric Investigations of Inorganic Compounds," 12th IUPAC Conference on Chemical Thermodynamics Joint Meeting with the 47 Calorimetry Conference, Snowbird, UT, August 17, 1992.
- O'Hare, P.A.G., "Thermochemistry of Metal Silicides," Sematech/NIST Workshop on Chemistry of CVD Processes in Semiconductor Manufacturing, Gaithersburg, MD, September 29, 1992. Invited
- Padmaja, S., "Temperature and Solvent Effects on Reactions of Inorganic Radicals," XXth Informal Conference on Photochemistry, Atlanta, GA, April 1992.
- Saini, R.D., "A Temperature Dependent Kinetic Study of the Reactions of OH Radical with CH_3Br , $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$, and $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$," American Chemical Society, Petroleum Division, Washington, DC, August 27, 1992.
- Stein, S.E., "The Status of the NIST/EPA/NIH Mass Spectral Database," NIST/EPA/NIH Mass Spectral Database Steering Committee, New Orleans, LA, March 1992. Invited

- Stein, S.E., "From One Extreme to Another: Application of Fundamental Chemical Principles to Coal Chemistry," Stoch Award Presentation, National American Chemical Society Meeting on Fuel Chemistry, San Francisco, CA, April 7, 1992. Invited
- Stein, S.E., "From One Extreme to Another: Application of Fundamental Chemical Principles to Coal Chemistry," Argonne/AMOCO Lecture Series, Argonne National Laboratories, Argonne, IL, May 21, 1992. Invited
- Stein, S.E., "Testing and Optimization of Mass Spectral Search Algorithms," ASMS National Meeting, Washington, DC, June 1992.
- Stein, S.E., "Testing and Optimization of Mass Spectral Search Algorithms," Symposium on Chemometrics, Montreal, Canada, July 16, 1992. Invited
- Tsang, W., "The Pyrolysis of 1,7-Octadiene and the Thermodynamic and Kinetic Stability of Allyl and 4-Pentenyl Radicals," Eastern States Section of the Combustion Institute, Ithaca, NY, October 15, 1991
- Tsang, W., "Status Report: Chemical Kinetic Data Base for Propellant Combustion," JANNAF Subcommittee Panel on Kinetics and Related Aspects of Propellant Combustion Chemistry, San Antonio, TX, October 28, 1991.
- Tsang, W., "Shock Tube Studies on the Formation and Destruction of Allyl and Propargyl Radicals," Department of Chemistry, Leeds, England, March 2, 1992. Invited
- Tsang, W., "Thermodynamic Properties of Alkyl Radicals," European Community Program on Combustion, Kinetic Data Panel, Abington, England, April 6, 1992. Invited
- Tsang, W., "Kinetic Stability of Unsaturated Hydrocarbons at High Temperatures," 201st National Meeting, Fuel Division, San Francisco, CA, May 5, 1992.
- Tsang, W., "Dioxin Destruction and Formation During Waste Combustion," Xth National Meeting on Combustion and Explosions, Moscow, Russia, September 15, 1992. Invited
- Tsang, W., "Semi-Empirical Methods for the Estimation of Chemical Kinetics Data," Sematech/NIST Workshop of CVD Processing in Semiconductor Manufacturing, Gaithersburg, MD, September 29, 1992. Invited
- Zhang, Z., "Atmospheric Lifetimes of Several Hydrofluoroethers," CHEMRAWN VII Conference, Baltimore, MD, December 1991.
- Zhang, Z., "Kinetic Studies of $\text{OH} + \text{C}_2\text{H}_2$ and $\text{OH} + \text{C}_2\text{H}_2 + \text{O}_2$ Reactions and of the Reactions of OH with CFC Alternatives," NIST, January 1992.

Zhang, Z., "Kinetic Studies of $\text{OH} + \text{C}_2\text{H}_2$ and $\text{OH} + \text{C}_2\text{H}_2 + \text{O}_2$ Reaction Systems Using Mass Spectrometry and Deductive Modeling," Brookhaven National Laboratory, Upton, NY, February 1992. Invited

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

None

4. Patent Awards and Applications

None

5. SRM Activities

39j Benzoic Acid (recertification)
2682a Sulfur Content in Coal (recertification)
2685a Sulfur Content in Coal (recertification)

6. SRD Activities

NIST/EPA/MSDC Mass Spectral Database (Update)
Chemical Kinetics (Update)
Thermodynamic Data Estimation (Update)
DIPPR (Update)
NIST Vapor Phase Infrared Database (New)

7. Calibrations

None

8. Committee Assignments

E.S. Domalski

The Calorimetry Conference (Chairman-Designate)
ASME Research Committee on Industrial and Municipal Waste
IUPAC Subcommittee on Thermodynamic Data (Secretary)

R.F. Hampson

NASA Panel for Data Evaluation
IUPAC Subcommittee on Gas Kinetics Data Evaluation for Atmospheric Chemistry
(Secretary)

J.T. Herron

Organizing Committee, Third International Conference on Chemical Kinetics
IUPAC Commission on Chemical Kinetics (Chairman)
IUPAC Subcommittee on Data for Low Pressure Plasma Chemistry
JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry
Washington Editorial Review Board

J.W. Hudgens

NIST Chemical Science and Technology Laboratory Colloquium Committee

R.E. Huie

Poster Session Committee - CHEMRAWN VII
Environmental Protection Agency Grant Review Panel
American Working Group in Physical and Material Sciences of the Indo-US
Subcommission on Science and Technology
Organizing Committee, Third International Conference on Chemical Kinetics (Chairman)

D.R. Kirklin

The Calorimetry Conference
National Organization for the Professional Advancement of Black Chemists and
Chemical Engineers
ASTM E-34 Committee on Waste Management

M.J. Kurylo

NASA Panel for Data Evaluation
International Scientific Steering Committee, Network for the Detection of Stratospheric
Change (Chairman)
CFC Replacement Strategy Review Committee, Department of Energy Gaseous Diffusion
Uranium Enrichment Operations

S.G. Lias

ASTM E-49 Committee on Computerization of Material Property and Chemical Data
Joint Committee on Atomic and Molecular Physical Data
American Society for Mass Spectrometry Measurements and Standards Committee

D. Neumann

AMSE Research and Technology Committee on the Properties of Water and Steam in
Thermal Power Systems

P.A.G. O'Hare

Scientific Organizing Committee, IUPAC Conference on Chemical Thermodynamics
IUPAC Commission on Thermodynamics (Chairman)

L.W. Sieck

Panel for Small Business Innovative Research Program of the U.S. Department of Energy

S.E. Stein

Air Pollution Modeling Instrumentation and Measurement Methodology Group.
Review Committee, Chemical Sciences Division, Oak Ridge National Labs
Alternate Councilor, Computers in Chemistry Division, American Chemical Society

W. Tsang

JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry
Review Committee, 24th International Symposium on Combustion
Organizing Committee, Third International Conference on Chemical Kinetics

9. Editorships

M.J. Kurylo

International Journal of Chemical Kinetics (Editorial Board)

S.G. Lias

Organic SEARCH (Structure, Energetics and Reactivity in Chemistry) Series (Chapman
and Hall)

P. Neta

Radiation Physics and Chemistry (Regional Editor)

P.A.G. O'Hare

The Journal of Chemical Thermodynamics (Editor)
Solution Calorimetry (Blackwells) (co-editor)
NIST Journal of Research (Editorial Board)

S.E. Stein

ACS Chemputer Guide (Editorial Board)

W. Tsang

Journal of Physical and Chemical Reference Data

10. Seminars

October 22, 1991

Dr. H. Cohen, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel "C-C Bond Formation Using Copper Ions as Catalyst: A Pulse Radiolysis Study." (Division Sponsor: P. Neta)

March 23, 1992

Dr. K. Bobrowski, Radiation Laboratory, University of Notre Dame, Notre Dame, IN, "OH-Induced Radical Processes in Sulfur Containing Amino Acids and Peptides." (Division Sponsor: P. Neta)

May 7, 1992

D. K. Norstrom, U.S. Geological Survey, Boulder, CO, "Geochemical Modeling and the Application of Thermodynamic Data to the Interpretation of Natural Water Chemistry." (Division Sponsor: D. Neumann)

May 8, 1992

Dr. K.S. Gupta, University of Rajasthan, Jaipur, India, "Oxidation of SO₂ in Aqueous Solutions Catalyzed by Metallic Particles." (Division Sponsor: R. Huie)

June 30, 1992

G. Nahor, Soreq Nuclear Research Center, Yavne, Israel, "Irradiation of Polymers." (Division Sponsor: P. Neta)

July 15, 1992

J.P. Mittal, Bhabha Atomic Research Center, Trombay, Bombay, India, "Pulse Radiolysis and Flash Photolysis Studies at BARC." (Division Sponsor: P. Neta)

September 17, 1992

Dr. B. Venkataraman, TIFR, Bombay, India, "Fast Reaction Studies on Radicals." (Division Sponsor: P. Neta)

September 28, 1992

Dr. D.F. McMillen, SRI International, "Chemical Factors in the Hydroprocessing of Heavy Petroleum." (Division Sponsor: W. Tsang)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

March 10, 1992

Meeting of the Steering Committee on the NIST/EPA/NIH Mass Spectral Database, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA (S.G. Lias and S.E. Stein)

August 16-21, 1992

Symposium on "Thermodynamics in the Industrial Environment," 12th International Union of Pure and Applied Chemistry (IUPAC) Conference on Chemical Thermodynamics, Snowbird, UT (P.A.G. O'Hare)

IV. Inorganic Analytical Research Division (834)

James R. DeVoe, Chief

A. Division Overview

The Inorganic Analytical Research Division conducts research and development for the accurate quantitative measurement of the chemical composition of materials. The effectiveness of our program is continually tested through participation in the Standard Reference Materials (SRM) program, where measurement results are meticulously compared within our laboratories at NIST and with outside laboratories. As a result, we constantly interact with industrial, government and university laboratories outside of NIST. These interactions have proven to be highly beneficial to both our staff and those of other laboratories.

The Division has strong programs for the development of analytical methods within each of our four groups: Atomic and Molecular Spectrometry, Electrochemical Methods, Mass Spectrometry, and Nuclear Methods. Each group provides an array of measurement methods that result in the identification of sources of measurement bias and leads to high accuracy when applied to the same SRM material. The Atomic and Molecular Spectrometry Group utilizes methods that are most common in commercial laboratories. Therefore, the publication of their procedures significantly elevates the quality of measurement science in a large segment of the analytical community. The Electrochemical Methods Group delivers critically needed standards in pH and conductance. The Mass Spectrometry Group provides measurements of very high precision and accuracy through the use of isotope-dilution procedures that cannot be used in most other laboratories because of their labor-intensive and costly nature. The Nuclear Methods Group uses techniques that employ nuclear phenomena, resulting in measurements that can be largely bias-independent from the methods used by other groups in the Division. Bias-independent methods do not share the same potential sources of measurement bias. Both individually and collaboratively, these groups make important contributions to measurement accuracy.

Direct collaboration with scientists outside of NIST substantially increased in FY92. The 37 guest scientists who worked in our laboratory came from industry (27%), academia (43%), and other government agencies (30%). In addition to our work in method development and SRM certification, we continue to perform a number of chemical analyses for organizations within and outside of NIST. In most cases, these analyses are for the purpose of establishing benchmark measurements for industrial or government clients and are not routine service analysis.

During the past year, the Division generated 369 Reports of Analysis, primarily from the certification of over 90 SRMs. The number of elements determined in each SRM ranged from one to more than 20. The certification of the suite of Spectrometric Solution SRMs continues to be one of our primary duties. We have developed classical measurement methods to narrow the uncertainty limits on certified values for many of these SRMs. Through collaborative studies

with several commercial laboratories, we established a 4% relative error in the stoichiometry of ammonium hexachlororhodate (III), commonly used to prepare standard solutions of rhodium. The results of this study culminated in the preparation of a highly-accurate rhodium solution SRM. Because of the importance of this element to the manufacture of automobile exhaust catalysts, the availability of this SRM will provide commercial buyers and sellers of rhodium metal with the solution to an analytical problem that amounts to millions of dollars. We have completed the certification of an important series of soil SRMs for over 20 elements. Two of the materials have elevated levels of toxic elements, and the SRM will provide for significant improvement in the characterization of environmental pollutants, such as lead in soil and dust. In collaboration with the Department of Housing and Urban Development and the Environmental Protection Agency, we have been working on a series of SRMs that are certified for lead content. We completed a lead-in-paint film which is used for the calibration of portable X-ray fluorescence instruments that measure nondestructively the lead in paint on the walls of buildings. Other SRMs under development include lead in paint powder and lead and other toxic elements in household dust. We have also enhanced the rigorousness of our Reports of Analysis, paying particular attention to providing a good estimate of measurement uncertainty and as much detailed information as possible about the measurement process.

The next paragraphs describe a Divisional perspective of selected accomplishments this past year for each of the groups. Some of these activities are summarized in more detail in the highlights to follow.

The Consortium for Automated Analytical Laboratory Systems will be entering its third year of existence in March of 1993. It has reached the point of maturity where it will be producing its first standards in communication protocol between the various components or Standard Laboratory Modules (SLMs) that make up an analytical system. The management of a consortium requires an extraordinary amount of time devoted to administrative matters and to building interest in the consortium. For example, the project manager has given over 20 off-site presentations at public and private meetings, and over 15 on-site presentations to visitors and VIP's. This is in addition to holding four 3 day workshops on modularization and two oversight board meetings for presenting a full review of the program. In order to expand the base and activities of the consortium a new program for associate members was established. This program is especially adapted to allow small businesses, particularly those dealing in software to participate in the concepts of automation design. With the current economic conditions, it is difficult to increase the general membership, and it is hoped that through this lower cost program, the effort can be expanded. In spite of such obstacles, the consortium has made excellent progress in establishing a philosophy of automation that is centered about the concept of modules, and the members have incorporated this concept into their own laboratories. We are currently evaluating the CAALS program with the intent of expanding the membership by enlisting the services of a marketing consultant. Certain aspects of the intermodular communication standard are requiring extensive debate among the members. Our immediate future task is to bring such discussion to closure.

The Atomic and Molecular Spectrometry Group placed heavy emphasis on the certification of SRMs again this past year. Over 15 elements in some 80 candidate materials were certified. Most notable among these are the spectrometric solutions which are used to calibrate instrumental methods.

The Fourier transform UV/VIS spectrometer is currently being used in a collaborative study with Iowa State University to generate ICP-OES reference spectra of the elements. A catalogue of spectra is planned with wavelength accuracy in the 0.3 parts per million range. The FT will be used to provide high accuracy wavelength calibration. An important contribution to the development of this instrument was the discovery that significant reduction in the ICP plasma flicker noise can be realized by utilizing electronic signals from a unique phase relationship between components of the electro-optical system that controls the interferometer. This provides for considerable increase in the dynamic range of the instrument. In our laboratory, studies are continuing on the measurement of glow discharge spectra with this instrument.

An important new activity in the Group is the incorporation of flow injection techniques as a sample preparation step prior to instrumental analysis. The intent is to automate some of the chemical separations so that they become modular in the CAALS sense.

The analytical application of laser spectroscopy has always suffered from a lack of low cost, reliable, easy to use lasers. Recent developments in tunable diode lasers have resulted in the prospect of meeting most of these requirements. In the past these devices have suffered from a lack of significant power output, but now with the layered geometry power has now improved to the point that significant output can be realized even after optically doubling the frequency. Studies are beginning for use of these lasers in fluorescence and photo-ionization.

The Electrochemical Analysis Group has devised a new direct current procedure for measuring electrolytic conductance. This method utilizes a four electrode procedure that is coupled with a high impedance voltage measurement. Results with this system compete well with the older AC impedance bridge system.

A very valuable electroanalytical instrument is the constant current coulometer. It has been used for many years to determine the purity and stoichiometry of the elements and compounds. However, it is an exceptionally tedious manual method. This instrument has been put under computer control and is almost fully automated. Current results show a measurable improvement of accuracy over the manual method.

The potential for high accuracy measurement in the Mass Spectrometry Group rests in the high precision with which isotope abundance ratios can be measured. This precision ranges from a few ten of parts per million when using thermal ionization with E/M focusing to a few parts per thousand when using an inductively coupled plasma source with quadrupole focusing (ICP-MS). The group has emphasized the use of ICP-MS recently because our experience over the past three years in evaluating its performance and in improving various parts of the system has shown it

to be suitable for the certification of Standard Reference Materials. Savings in time without sacrificing accuracy can be realized in some selected cases by performing multiple isotope spiking, and less frequently an external standard can be used.

Element assay and purification procedures have been completed, preliminary to the determination of the atomic weight of zinc. Zinc turns out to be one the least well known atomic weights, and we expect to improve its accuracy by a factor of ten. In addition to the importance of having accurately known atomic weights, this project provides the group with the opportunity to develop their expertise for the certification of SRMs by isotope dilution. Some studies have been completed on the thermal ionization procedure that will be used for the mass spectrometry. The trick is to generate sufficient ion beam current with enough filament loading to reduce interference effects. Typically, at the current level of funding, an atomic weight measurement will require five years. This will be the 17th element for which the atomic weight has been determined.

While the group has terminated a project in the design and fabrication of mass spectrometers, we have sufficient spare parts of the original NBS (twenty-five year old design) instrument to assemble two additional spectrometers. As an indication that their performance is still competitive with contemporary designs, the Centre Bureau for Nuclear Measurements, Geel, Belgium has requested to have one of these spectrometers. In the past few years we have purchased several commercial spectrometers. The commercial magnetic sector thermal ionization instrument which we have purchased can measure competitively with the NBS design with the exception of those cases of elements with nuclides of very low isotopic abundance requiring an instrument with large dynamic range.

A large part of the Nuclear Methods Group's efforts has been directed toward the analytical applications of cold neutrons. We have designed and constructed state-of-the-art instruments for both PGAA, neutron depth profiling (NDP), and instrumentation for the focusing of neutrons. The competence building project on the focusing of neutrons made significant progress this past year. A collaboration with X-ray Optical Systems, Inc. (a small company which received a NIST ATP contract) and the Kurchatov Institute in Moscow resulted in a demonstration for the first time of focusing neutrons via a glass capillary. The combination of our invention of a spatially sensitive real-time neutron detector with their invention of the fabrication of a glass fiber lens resulted in the major breakthrough. The results of this work were published this year (*Nature* 357, 391-393 (1992)).

The prompt-gamma activation analysis (PGAA) instrument continues to be improved. This facility will allow accurate measurements of low levels of a number of elements including hydrogen. A longstanding problem with high temperature alloys is their sensitivity to embrittlement caused by the presence of hydrogen. Quantitative analysis of hydrogen is very difficult to do. Recent measurements of hydrogen in turbine blades using PGAA indicated an elevated hydrogen concentration in the regions of failure.

For NDP, a new highly versatile 60-cm diameter chamber has been designed for ultra-high vacuum capability. The instrument's improved sensitivity resulted in the measurement of the depth of boron distribution in diamond films which are being considered as a new semiconductor material. We plan to incorporate time of flight measurements in this instrument for the purpose of improving the depth resolution. By measuring the heavy residual nucleus of a light element such as nitrogen, it may be possible to measure distributions of depth to a maximum of ten nanometers with a resolution of a fraction of a nanometer.

Significant accomplishments have been made on the compositional metrology side of the Group's efforts. An important paper was published on the trace element composition of marine mammal livers which was done in collaboration with NOAA and EPA who support the Specimen Bank. A four year international study in collaboration with the IAEA involving the measurement of trace elements in foodstuffs was completed this year. This group serves a special function among the laboratories of the world performing neutron activation analysis by conducting inter-laboratory comparisons of trace element concentrations in botanical and biological materials, and recently, they have initiated a study of the trace element measurements in silicon.

**B. Selected Technical Reports
(Inorganic Analytical Research Division)**

1. The Development of New Atom Sources for Laser Resonance Ionization Mass Spectrometry

J.D. Fassett, L.A. Moore, P. Crescioli (Eastern Analytical, Inc.), X. Xiong (Eastern Analytical, Inc.), and J.M.R. Hutchinson (PL)

Resonance ionization mass spectrometry (RIMS) is a technique that combines the ability of laser radiation to photoionize gas phase species selectively and efficiently with the mass resolution capabilities of mass spectrometry. We have been using this technique with the production of atomic species from resistively heated filaments. Thermal vaporization, despite its inherent inefficiencies, has continued to provide extremely useful analytical measurements: one example is the vanadium isotopic ratio measurements described elsewhere in this report. We have begun experiments this year with two alternative sources of gas phase atomic species, the glow discharge and ion sputtering.

A glow discharge cell was built and installed in the source chamber of the NIST 90° magnetic sector RIMS instrument and modifications were made to handle the gas load in the flight tube. The element tin was measured first in the glow discharge mode. Relatively large signals with excellent mass resolution and appropriate isotopic abundances were observed. The first experiments during which a RIMS signal was observed were a failure, so a calibration was done by returning to a thermal source of Sn. Difficulties were still encountered in the observation of an atomic beam of tin from the glow discharge. Photoions of tin were observed, but without the selectivity of the resonance ionization. These results suggest that a relatively large fraction of the tin species is produced in clusters which are photodissociated and ionized non-selectively by the laser. Experiments to use RIMS to characterize the glow discharge process and explore the glow discharge atom/ion source for mass spectrometry are continuing.

The use of pulsed ion sputtering to optimize the overlap of the atomization and ionization processes has long been considered the way to improve the inherent sensitivity of RIMS. The problem with sputtering as done by other laboratories has been the calibration of the process. We plan to continue to do isotope dilution with minimal sample processing to overcome the problem of calibration. This strategy reduces the requirements placed on the sputter source specifications. A saddle-field ion source was purchased and tested. Simple in design and operation, this ion source produced a maximum of 20 microamps of current with a divergence of 3.8°. It was installed on an existing port of our RIMS I instrument, perpendicular to both the laser beam and ion optical axis. For the first experiments, a rhenium target was used, and a very large RIMS signal was immediately observed, whose magnitude was proportional to the sputter beam intensity. Thus, this source appears adequate. The design of a new mounting arrangement is in progress, which will allow pulsing of the sputter beam and suppression of sputtered ions and fast atoms produced by the saddle-field ion source.

2. Evaluation of Industrial Processes and High Purity Materials

J.R. Moody and P.J. Paulsen

The Analytical Mass Spectrometry Group has provided consultative services to industry for a number of years. These services usually require analytical services of very high quality not ordinarily available from commercial analytical laboratories. Alternately, the services involve providing a complete environment for the evaluation of a process or a product. Since most of these services produce proprietary information, we will present two recent examples of NIST technical assistance in a generic way.

The first involves the Millipore Company, a large manufacturer of ultrafilters, de-ionized water systems, and other laboratory devices for analytical, bio-technology, and semi-conductor applications. Millipore had developed a novel process for reagent purification, but lacked the analytical services to fully evaluate the commercial usefulness of the process. NIST provided the clean lab space to set up a bench top demonstration of the process as well as to perform the necessary analytical sample preparations. These samples were then analyzed by ICP/MS (inductively coupled plasma/mass spectrometry) for more than 40 elements at the part per billion (ng/g) concentration level in the process fluids. These analyses showed which elements were purified in the process fluids as well as which conditions gave the best results.

The second example involves the Enfield Industrial Co., a multi-national manufacturer of commercial piping systems. The company needed to know the contamination levels of its piping systems to satisfy the requirements of their semiconductor customers. After discussions about the experimental design, NIST provided the experimental set-up to characterize a polypropylene piping material exposed to ultra-pure water (less than ng/g impurity levels for cations). NIST has completed the leaching experiments for the materials provided and will soon be able to advise the company of the contamination levels as determined by ICP-MS measurements. This experiment was closely related to prior NIST experience in contamination from plastics and thus benefited the customer in the experimental design.

In both cases, NIST provided sophisticated laboratory capabilities, ultratrace measurement expertise, and appropriate experimental designs in order to give the customer an evaluation of their problem. Occasionally these services lead to another set of experiments at NIST or suggest a more fruitful approach for the manufacturer.

3. Comparative Strategies for Accurate Measurement of Vanadium (V) by IDMS With Interferences from Titanium and Chromium

J.D. Fassett, E.S. Beary, and X. Xiong (Eastern Analytical, Inc.)

One of the major sources of potential systematic error in isotope ratio measurement is mass spectrometric isobaric interferences. The accurate measurement of vanadium (V) isotopic ratios provides a significant test of our ability to control interferences. Vanadium is an element with two stable isotopes, but is principally ^{51}V ($^{51}\text{V}/^{50}\text{V} = 400$). The minor isotope of V is interfered with by isotopes of both titanium and chromium. A procedure has been developed in our laboratory for determination of V by isotope dilution and thermal ionization mass spectrometry (TIMS). The interferences limit the capability of this method, especially in its application at the parts-per-billion level, or at the natural levels in serum and foodstuff.

Experimental strategies for controlling the interferences of chromium and titanium in the measurement of $^{50}\text{V}/^{51}\text{V}$ were investigated. These strategies were: (1) Purification of the analyte, V, before mass spectrometric measurement; (2) Dynamic correction of V by measurement of Ti and Cr; and, (3) Element selective ionization using laser resonance ionization (RIMS). These experiments were done in the course of determining the V content in tomato leaves, SRM 1573a, which is in the process of being certified. Spiked samples were split, and isotopic ratios were made by both TIMS and RIMS. The various strategies for interference control have advantages and disadvantages, and their applicability is strongly dependent upon the amount of analyte available. For instance, the use of chemical separations introduces two concerns, contamination (or blank) and recovery. For TIMS, the accuracy of interference corrections becomes more and more problematic as the magnitude of these corrections increase. RIMS is inherently less precise than TIMS and, also, there is wider recognition now of isotope effects in photoionization that can affect the fidelity of ratio measurement.

The concentration of V in tomato leaves using thermal ionization was 824 ppb (± 10 ppb). The interference corrections ranged from 10-40% for titanium and 2-14% for chromium. The raw data was analyzed to estimate the systematic errors caused by the interference corrections. The result was a revised concentration of 835 ppb (± 0.3 ppb). RIMS is an elementally selective ionization technique that utilizes tunable lasers for multiphoton ionization. No interference corrections were necessary using RIMS. The samples were heated in a mass spectrometer in a similar manner as done for thermal ionization. The measured ratios were normalized to the TIMS values using a series of calibration samples ($\text{RIMS}/\text{TIMS} = 0.9830 \pm 0.0134$). The concentration determined using RIMS was 828 ppb (± 14 ppb). These results illustrate the applicability of new methods and procedures to solve increasingly difficult problems of analysis.

4. Multi-element Certification Measurements in SRMs by Inductively Coupled Plasma Mass Spectrometry With and Without Isotope Dilution Mass Spectrometry

E.S. Beary and P.J. Paulsen

ICP-MS has become a powerful analytical tool in inorganic analyses since its commercial introduction in 1983. Its rapid, scanning, multi-element capabilities offer distinct advantages over traditional mass spectrometry for many analytical applications. Quantitation best suited for ICP-MS takes advantage of the instrument capability for accurate and precise ratio measurements.

Two different methods of quantitation were used with the ICP-MS: an internal standard technique and isotope dilution (IDMS). In both cases analytical data are generated based on measured ratios. ICP-MS quantitation based on signal intensity (e.g., standard addition or the use of external standards) depends upon the stability of the absolute signal intensity. This approach to quantitation is problematic in the ICP-MS because the signal transmission drifts with time. The addition of an internal standard minimizes the effects of this drift since the relative transmission of the standard versus the analyte normalizes the quantitative data. However, the stability of the relative transmission must be verified. In IDMS, an enriched isotope of the analyte serves as an ideal internal standard since both the standard and the analyte have exactly the same chemical properties, exhibiting identical chemical behavior from the sample preparation to instrumental analysis. Under carefully controlled conditions, only isotope dilution is immune to all shifts in signal level since an isotopic ratio of single element is used, and not a ratio between elements. In IDMS ratio measurements are precise to about 0.2%.

The concentrations of Pb, Cd and Zn were determined by isotope dilution (IDMS) in renewal SRM 2676d, Toxic Metals on Filters. The element manganese, mononuclidic at mass 55, was certified using ^{59}Co as an internal standard in this filter SRM. In addition, Pt and Pd were determined in two new autocatalyst SRMs 2556 and 2557 by IDMS, while Rh, at mass 103, was quantified versus ^{115}In .

Ratio measurements between two different elements were made in the ICP-MS internal standard technique used to quantify the Mn and Rh in these new SRMs. However, tracking the analyte versus the internal standard during the entire analytical scheme is a requirement that can be difficult. The $^{55}\text{Mn}/^{59}\text{Co}$ ratio was measured in the filters with precision approaching 0.2%. Accurate and precise quantitation of the Mn versus an internal standard was possible in the filter SRM for the following reasons: only the added elements (Pb, Cd Zn and Mn) were present at significant levels in the samples, and the absence of a molecular ion interference at mass 55 could be easily verified; the filter material was readily decomposed, and therefore, the solution as presented to the ICP-MS was essentially matrix free. Under these conditions the internal standard technique provided analytical precision similar to that of IDMS, generally better than 0.5%.

Quantitation of Rh versus In in the autocatalysts was more demanding. The $^{103}\text{Rh}/^{115}\text{In}$ ratio measurement was poorer than those obtained for the IDMS quantitation of Pt and Pd in the same material, presumably due to the complex inorganic matrix. In addition, the process of verifying the absence of interferences at mass 103 was tedious and relied on the meticulous preparation of synthetic standards. Isolation of the Rh was desirable, however, no separation was quantitative or sufficiently reproducible for high accuracy results. In these SRMs the internal standard technique did provide quantitation of this difficult mononuclide. However, IDMS quantitation of the Pt and Pd provided better accuracy and precision.

5. Preparation and Certification of a Rhodium Spectrometric Standard Solution

C.M. Beck III, T.A. Butler, M.L. Salit, and R.L. Watters, Jr.

Comparisons among commercially-produced rhodium solution standards have shown that they differ among themselves by as much as 10% relative. For commercial buyers and sellers of rhodium metal, this translates into analytical errors that can amount to tens of millions of dollars per year on the world rhodium market. Therefore, it is important that an accurate solution standard of this precious metal be made available.

An accurate rhodium solution standard is difficult to prepare because rhodium metal is almost impossible to dissolve in any acid or acid mix, and available water-soluble rhodium salts are seldom, if ever, stoichiometric. A dual-path approach was developed for the preparation of an accurate rhodium solution standard. The first path was the classical gravimetric assay for rhodium of a high-purity soluble rhodium salt which subsequently was dissolved in 10% HCl to prepare an accurate standard solution. We used commercially available ammonium hexachlororhodate (III) since it could be dried to constant weight, and was low in trace impurities. The gravimetric assay was carried out in a Rose crucible, which consists of a 30-mL-size quartz crucible, fitted with a quartz lid with a central hole, through which a quartz gas-entry tube is inserted. (An illustration of a Rose crucible appears in Quantitative Analysis by Tredwell and Hall.) The ammonium hexachlororhodate (III) was dried to constant weight at 110 °C, and a 1g specimen was accurately weighed directly into the Rose crucible. The crucible was slowly heated in a muffle furnace to 800 °C to convert the salt to rhodium oxide. After cooling, the Rose crucible was assembled with its lid and gas-entry tube and, after purging thoroughly at room temperature with argon, a flow of hydrogen was introduced. The crucible was gently and carefully heated with a low flame until the rhodium oxide was reduced to rhodium metal, evidenced by the sudden appearance of condensed water on the inside of the lid. The crucible then was heated to the full heat of a Meker burner for one hour to reduce as completely as possible any remaining traces of oxide. This rhodium metal was weighed, the impurities were determined (which amounted to 0.075%), and the weight of the impurities was deducted from the weight of the impure metal. As suspected, the chemical formula (which gave a calculated value of 27.83% rhodium) was not correct. Seven replicate determinations were made and a

rhodium assay of 28.97% $\pm$ 0.07% was obtained. Based on this assay, a 1,000- μ g/mL rhodium solution standard in 10% HCl was prepared.

In order to confirm the accuracy of this rhodium solution standard, a second path was taken by synthesizing a different soluble rhodium salt from high purity rhodium metal. Exactly 0.1000g of high-purity rhodium metal was weighed into a small quartz (30 mm long, 15 mm wide, and 10mm high) boat which was placed in a cold tube furnace. After establishing a flow of chlorine gas, the furnace was heated for 2 hours at 650 °C while maintaining the flow of chlorine. After cooling, 1.000 g of sodium chloride was placed over the partially chlorinated rhodium metal, and the boat was placed back into the fully-cooled tube furnace. After reestablishing the flow of chlorine gas, the sample was heated to 790 °C for 3 hours. After cooling, the resulting ruby-red melt [presumably containing the rhodium as water-soluble sodium hexachlororhodate (III)] was dissolved in water and brought to 100.0 mL in 10% HCl. This produced a second 1,000- μ g/mL rhodium solution standard.

Demonstrating the indistinguishability of both 1,000- μ g/mL rhodium solution standards confirmed the accuracy of the original rhodium solution standard. An accurate one-to-ten dilution of each 1,000- μ g/mL solution standard was made using the same glass-transfer pipet. The final sodium concentration and total acidity were carefully matched, and each standard was spiked with 50 μ g/mL indium and 50 μ g/mL scandium. The indium served as the primary internal standard and the scandium served as a short-term, noise-rejection internal standard for both rhodium and indium. Comparison of these two solutions by ICP-OES showed them to be indistinguishable to within 0.2% relative.

Based on this fact we conclude that we now have an accurate rhodium solution standard. The accuracy is based on a gravimetric rhodium assay of the water-soluble rhodium salt used to prepare the solution standard, and the accuracy is confirmed by comparing this solution to an independent rhodium solution standard made from a known weight of high-purity rhodium metal.

6. Tunable Diode Lasers for Chemical Analysis Using Laser-enhanced Ionization

G.C. Turk, L. Hollberg, and R. Fox (PL)

The past decade has seen considerable advances in the field of trace chemical detection based on the use of laser spectroscopy. A variety of new spectroscopic methods has been developed and applied to challenging problems in analytical chemistry. However, these laser-based methods of analysis have not gained wide acceptance among analytical chemists, and are found only at a few research institutions around the world. This lack of general acceptance results directly from the complexity and expense of the required laser systems -- generally wavelength tunable lasers using organic dyes. The recent availability of inexpensive and rugged tunable diode lasers offers hope for a wider application of laser spectroscopy within the field of chemical analysis. This point has been recognized by the research community in the field of analytical laser spectroscopy. An

extensive program in the development of diode lasers for analytical applications is in place at the Institute of Spectrochemistry and Applied Spectroscopy in Germany under the leadership of Professor Kay Niemax. We have now entered the diode laser field in a collaborative effort with laser physicists from the NIST Time and Frequency Division in Boulder. The Boulder group has extensive experience in the application of diode laser spectroscopy for fundamental applications in atomic physics. Together, we have performed what we believe to be the first use of visible and near-IR tunable diode laser for laser-enhanced ionization (LEI) spectroscopy in a flame.

Laser-Enhanced Ionization is based upon the enhanced rate of collisional ionization of the excited atoms produced by the absorption of laser radiation relative to ground state atoms. Elemental specificity is provided by the selective excitation of the element of interest using laser radiation tuned to an atomic transition wavelength of the element. The enhanced ionization signal is detected by measuring the increased electrical conductivity of the flame with probe electrodes.

We have measured LEI signals of rubidium and cesium in an air-hydrogen flame. These two elements are the most amenable to diode laser excitation because they have strong ground state transitions in the far red and near-IR at 780.023 nm and 852.124 nm respectively, where diode lasers are readily available. Also, the low ionization potential of these elements favors LEI. Diode lasers were used with and without the use of an external laser cavity surrounding the diode chip. The use of an external cavity offers more complete wavelength coverage for a particular diode, but adds to the complexity and expense of the laser. The laser light was mechanically chopped at 2 kHz before entering the flame, and the LEI signal was detected with phase-sensitive detection synchronized with the chopper.

Limits of detection were determined for the two elements studied--0.2 ppb for Cs and 0.3 ppb for Rb. These detection limits are comparable to those achieved using a considerably more complex and expensive krypton ion pumped dye laser. The limiting source of noise was alkali metal contamination in the flame. The most notable attribute of these diode laser LEI measurements is not the sensitivity, but rather the simplicity of the instrumentation. The use of conductivity rather than optical detection, and the simplicity of the laser, results in a very rugged instrument.

The challenge for future development of diode laser LEI, and other diode laser spectroscopic methods, is expansion of the wavelength coverage of diode lasers to shorter wavelengths. Future experiments are being planned using a frequency-doubled diode laser that operates at blue wavelengths, which is available at NIST-Boulder.

7. The Determination of Stoichiometry of Silicon Telluride for the Determination of Its Standard Molar Enthalpy of Formation

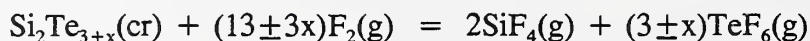
C.M. Beck III and P.A.G. O'Hare (833)

In connection with the investigation of the thermodynamic properties of the silicon + tellurium system, highly precise and accurate assays for both elements are needed. It has been known for some time that the previously believed existence of SiTe and SiTe_2 was incorrect, and that the only solid silicon telluride that exists is Si_2Te_3 . Since there is evidence, however, that Si_2Te_3 can be nonstoichiometric, it is essential to ascertain the chemical composition of calorimetric samples used in the determination of the thermodynamic properties of silicon + tellurium.

Major details of the determination of silicon content are as follows. Carefully weighed specimens (0.4 g, corrected for SiO_2 impurity) of Si_2Te_3 were removed from the glovebox and immediately dissolved in aqua regia on a warm hotplate ($< 100^\circ\text{C}$) for several hours. The sample was taken to dryness on a 100°C hotplate to dehydrate the SiO_2 formed by the oxidation of the Si_2Te_3 . The SiO_2 was treated with hot HCl and collected on ashless filter paper. The filtrate was reserved for subsequent determination of dissolved Si by ICP spectrometry. The filter paper containing the precipitate was carefully ignited to constant weight in a small porcelain crucible. A platinum crucible was not used because of the danger of ruining it with tellurium contamination. The impure SiO_2 was transferred to a small tarred Teflon beaker and SiO_2 was volatilized using HF , leaving the nonvolatile impurities behind. After cooling, the Teflon beaker was weighed to determine the weight of impurities. The weight of the impure SiO_2 , minus the weight of the impurities, plus the equivalent weight of SiO_2 in the filtrate (determined by ICP-OES spectrometry) gave the amount of Si in the sample in terms of SiO_2 . Three replicate assays gave a mean value of 12.75% Si; the theoretical result for exactly stoichiometric Si_2Te_3 is 12.80%.

Major details of the determination of tellurium are as follows. Carefully weighed specimens (0.12 g corrected for SiO_2 impurity) were removed from the glovebox and dissolved on a warm hotplate under 100°C to avoid volatilizing tellurium chloride. The cover glass was then replaced by a ribbed cover glass and the sample taken to dryness. It was important that this also be done at or below 100°C , so as not to risk losing volatile tellurium chloride. The residue was dissolved in 20 mL of 2 mole/L HCl and 50 mL of H_2SO_4 (1+1), and 10 mL of 30% (wt/vol) MnSO_4 was added. After diluting to 100 mL, the solution was cooled to room temperature. Using a calibrated pipet, 50.00 mL (a calculated excess) of 0.4500 mole/L $\text{K}_2\text{Cr}_2\text{O}_7$ (SRM 136e) was added and the solution set aside for 15 minutes to allow the oxidation-reduction reaction to take place. The excess $\text{K}_2\text{Cr}_2\text{O}_7$ was back-titrated with standardized 0.075 mole/L $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ using ferroin indicator. The weight of Te in the sample was calculated from the amount of dichromate consumed. The average for three replicate Te assays was $87.09\% \pm 0.20\%$. The theoretical result for exactly stoichiometric Si_2Te_3 is 87.20%.

Based on these data, the material has a formula of $\text{Si}_2\text{Te}_{3.01 (\pm 0.01)}$. It was necessary to determine with great care the value of x in $\text{Si}_2\text{Te}_{3 \pm x}$ because, in considering the reaction:



both the molecular weight of $\text{Si}_2\text{Te}_{3 \pm x}$ and $(3 \pm x)\Delta_f H_m^\circ(\text{TeF}_6)$ enter crucially into the derivation of $\Delta_f H_m^\circ(\text{Si}_2\text{Te}_{3 \pm x})$ from the experimentally measured specific energy of combustion.

8. Automated Flow-Injection Analysis for the Determination of Mercury in Standard Reference Materials

M.S. Epstein and R. Saraswati (Ministry of Science and Technology, India)

The recent acquisition of a commercial flow-injection analysis system (FIAS) has tremendously increased the quality and throughput of cold-vapor mercury determinations in our laboratory. The FIAS provides a unique flexibility to the sample preparation and introduction steps of this analytical measurement method by combining several different operations (i.e., preconcentration, separation, gas-generation) into a united and dynamic flow system which is easily automated. In the case of mercury determination by the cold-vapor atomic absorption method, the FIAS automates sampling, reagent addition, and gas-generation procedures.

Results were obtained for five proposed standard reference materials (SRMs) covering a range of concentrations from 0.03 $\mu\text{g Hg/g}$ to 50 $\mu\text{g Hg/g}$. These included SRM 1570a (Spinach), SRM 1573a (Tomato Leaves), SRM 1633b (Fly Ash), SRM 113b (Zinc Ore), and SRM 8400 (Sewage Sludge) as well as associated control samples. Total uncertainties for these measurements varied from less than 1% for higher mercury concentrations to about 20% for ultratrace mercury levels.

The high precision of the FIAS mercury determinations allowed a more careful evaluation of bias resulting from sample preparation and matrix interferences, and led to a redesign of sample preparation procedures that had been standard for over twenty years.

9. High-accuracy Wavelength Measurements by Fourier Transform Spectroscopy for Inductively-Coupled Plasma Optical Emission Spectrometry

J.C. Travis, M.L. Salit, and M.R. Winchester

The inductively coupled plasma (ICP) has proven to be the most useful spectrochemical plasma ever developed for quantitative analysis. Over the last two decades, ICP Optical Emission Spectrometry (ICP/OES) has become a widely-used tool for the determination of minor and trace elements in complex samples. Commercial development of ICP/OES has recently been

stimulated by the advent of sensitive imaging detectors and more powerful and cost-effective microprocessors, but instrument performance is increasingly limited by spectral databases which are inadequate for such "smart" implementations. In 1987, a workshop on "Needs for Fundamental Reference Data for Analytical Atomic Spectroscopy" resulted in a special issue of *Spectrochimica Acta B* (43B(1), 1988). In this issue, the editor P.W.J.M. Boumans concluded from the compilation of a questionnaire that "It is of substantial economical interest to solve in the next 5 years a major problem of analytical atomic emission spectrometry: compiling and managing the data needed for adequately dealing with line selection and spectral interferences." (His emphases.) Taken in the context of the Workshop discussion, "compiling" in this case includes the generation of new data tables. In fact, Royce Winge of Ames Lab [private communication] has found that of the 150 Nd ICP lines observed by the Ames Lab in the 5-nm region centered at 303 nm, only 7 are reported in one widely-used wavelength table, 57 in another, and none in a third.

Ames Laboratory, one of the original development centers for the ICP, has been assembling an ICP spectral atlas over the last few years, and will collaborate with us for the final wavelength calibration. Whereas the diode-array grating spectrometer at Ames is capable of registering over five orders of magnitude in dynamic range, the instrument requires wavelength calibration for each 5-nm operational wavelength interval. The use of literature values for prominent spectral lines is unreliable, since the data may represent substantially different plasma properties than the ICP (pressure/Stark shifts, etc.). The NIST Fourier Transform Spectrometer (FTS), provides the essential characteristic of high-accuracy wavelength calibration to complete this project.

The FTS is operated at 0.06 cm^{-1} resolution, which fully resolves ICP lines and yields more-than-adequate self-apodization. To achieve the required wavelength accuracy, the FTS must be calibrated to correct for the "cosine error" between the optical axis of the signal beam and that of the reference stabilized HeNe laser. A "see-through" Fe hollow cathode lamp aligned on the optical axis between the ICP and the FTS is used to calibrate the FTS to an estimated accuracy of at least 3 parts in 10^7 . Steps are being taken to improve the systematic error in line position determination to about 1 part in 10^7 with the FTS. Following these improvements, high accuracy spectra will be acquired for a small suite of line-rich elements, capable of providing a spectral line of adequate signal-to-noise ratio (>25) for each spectral segment (approximately 5 nm) employed by the Ames spectrometer. These lines will then be curve-fitted to provide a complete table of calibration transfer standards. Operation of the instrument at Ames will then require the acquisition of a reference calibration spectrum every time the grating is repositioned.

The observed (fitted) positions for a suite of strong Fe lines determined by the NIST FTS have been compared to values determined by the Imperial College FTS to establish a precision of about 3 parts in 10^8 for spectral lines for which the signal-to-noise ratio exceeds ~ 100 . A similar correlation between Fe spectra acquired on the NIST FTS and the Ames spectrometer yields a precision of about 3 parts in 10^7 , reflecting the lower resolution of the conventional spectrometer. Nevertheless, the precision and accuracy of about 0.1 pm in the calibrated spectrometer represents a significant improvement over prior databases for the ICP.

The spectral atlas is expected to cover about 70 elements, from 185 to 434 nm, with a dynamic range approaching 10^6 . Line positions and intensities for well-specified plasma and viewing conditions will be available in both printed and computer-readable form. Though the question of intensity calibration of the Ames instrument over the entire spectral range has yet to be resolved, the importance of intensity for chemical analysis is that over small spectral ranges, line intensity per unit species concentration represent the same scale for all elements reported. Such intensity correspondence is necessary for accurate interference correction algorithms to be implemented in state-of-the art ICP spectrometers.

10. The Determination of Dissociation Constants and Activity Coefficients Needed for New pH Buffer Standard Reference Materials

P.A. Berezansky, Y.C. Wu, D. Feng (Guangzhou Research Institute of Non-ferrous Metals, Peoples' Republic of China), and W.F. Koch

The compound BES (N,N-bis[2-Hydroxyethyl]-2-aminoethanesulfonic acid) has been studied as a proposed third standard buffer at pH 7.1. This new standard is designed to be used in conjunction with two certified standard reference materials, HEPES (N-[2-Hydroxyethyl]piperazine-N'-ethanesulfonic acid) at pH 7.5 and MOPSO (3-[N-Morpholino]-2-hydroxypropanesulfonic acid) at pH 6.9, in three point calibration bracketing of the pH of physiological fluids.

The first buffer measured was designed with an ionic strength that approximates seawater and physiological fluids. It consists of the amino acid ($Z^{\pm}$), its sodium salt (Z^{-}), and sodium chloride (Cl^{-}), where $m_{Z^{\pm}} = m_{Z^{-}} = m_{Cl^{-}} = 0.08$ molal. The other buffer contains $Z^{\pm}$ and Z^{-} where $m_{Z^{\pm}} = m_{Z^{-}} = 0.05$ molal.

The activity coefficient of the chloride ion, $\gamma_{Cl^{-}}$, is necessary for the pH determination. The $\gamma_{Cl^{-}}^{\circ}$, the activity coefficient of the chloride ion in pure NaCl solution, is found by the Debye-Hückel extended equation. The presence of $Z^{\pm}$ changes the value of $\gamma_{Cl^{-}}$. This effect can be found by using a sodium ion selective electrode and an Ag, AgCl reference electrode to measure solutions of $Z^{\pm}$ and NaCl, where $m_{Z^{\pm}} = m_{Cl^{-}}$ and $m_{Z^{\pm}}$ is the same concentration found in the appropriate buffer. This is compared to the same measurement of a solution of pure NaCl at the same $m_{Z^{\pm}}$.

The first method of pH determination involved the measurement of the second acid dissociation constant, K_{2A} , by measuring the emf of a solution of $Z^{\pm}$, Z^{-} , and NaCl with a standard hydrogen electrode and an Ag, AgCl electrode in an electrochemical cell without liquid junction. The activity coefficients of the amino acid, $\gamma_{Z^{\pm}}$, and its sodium salt, $\gamma_{Z^{-}}$, are also determined. The following equation was used:

$$pH = -\log a_{H^{+}} = pK_{2A} + \log(m_{Z^{-}}/m_{Z^{\pm}}) + \log(\gamma_{Z^{-}}/\gamma_{Z^{\pm}})$$

The same cell used to determine the pK_{2A} is used to determine the pH by the second method by the following equation.

$$pH = -\log a_{H^+} = (E - E^\circ)F/RT \ln 10 + \log m_{Cl^-} + \log \gamma_{Cl^-}$$

The pH determined by these two methods agreed to within 0.01 pH of each other. When the BES was measured with a pH meter and a glass combination electrode standardizing with the HEPES and MOPSO buffers, the results were very close to the previously determined values.

Electrochemically determined pK_{2A} of amino acids and pH of their buffers at 25°C.

<u>Amino Acid</u>	<u>pK_{2A}</u>	<u>pH 0.05 m Buffer</u>	<u>pH 0.08 m Buffer</u>
HEPES	7.562	7.503	7.516
MOPSO	6.929	6.867	6.865
BES	7.165	7.114	7.105

11. High-accuracy Automated Coulometry for the Certification of SRMs

Y.C. Wu, D. Feng (Guangzhou Research Institute of Non-Ferrous Metals, Peoples' Republic of China), W.F. Koch, and L.A. Holland

Coulometric methods have been used at NBS/NIST for assays of high-purity acidimetric, oxidimetric, and halide standards for over 20 years. Advantages of these procedures include accuracies of better than 0.01% relative, absolute basis (Faraday's Laws), and direct determination of the major matrix component.

Major efforts in FY 1991 and 1992 have been directed toward the total automation of these procedures, thereby increasing productivity and reproducibility while reducing the degree of operator dependence and tedium. For SRMs, the goal is to make automated, high-precision coulometry available for all future certifications where coulometry is applicable.

In FY 1992, five SRMs were acceptance-tested and/or certified using high-accuracy automated coulometry: three acidimetric SRMs (39j Benzoic Acid, 723b Tris, and 924a Lithium Carbonate); Potassium Dichromate (SRM 136e); and Potassium Chloride (SRM 999a/918a). In each case, accurate analyses required solutions to compound-specific requirements before the SRM analyses could be performed. These are outlined below.

For the acidimetric titrations, the basic titration equation (moles OH^- added vs pH) was derived and incorporated into the program. Each incremental titration time is predicted from this equation, based on the preceding pH values and the goal pH value. This process is iterated to reach the endpoint region in the optimal time. The exact endpoint is then determined by a cubic curve fit of 10 points immediately surrounding the endpoint. This achieves increased accuracy

and precision compared to a single pH measurement. Back-titrations for basic SRMs (Tris, Li_2CO_3) are effected using the same principle, with the necessary introduction of the excess acid (HCl) included in the sample introduction step.

In the case of benzoic acid, slow dissolution of the acid resulted in large positive errors. This problem was resolved by agitating the solution after the main (high-current) titration until the solution pH reached a stable value, indicating total dissolution.

For the oxidimetric and halide titrations, the amperometric endpoint detector was adapted to automated operation. In the completed system, the indicator electrodes are automatically disconnected from the associated electronics except during the endpoint measurements, thereby avoiding systematic errors from ground loops. Averaging and statistical analysis routines were incorporated into the program to improve the signal-to-noise ratio of the endpoint measurements and provide an error estimate.

The $\text{K}_2\text{Cr}_2\text{O}_7$ titrations required two additional features. A pre-titration step was added to reduce the excess $\text{K}_2\text{Cr}_2\text{O}_7$ included in the supporting electrolyte to oxidize trace impurities. Deaeration of the cell solution was also implemented, to remove dissolved O_2 . This required automating the procedure for raising and lowering the deaeration frits to avoid analyte loss.

The halide titrations also required two special features. An automated timing procedure for rinsing the cell frits was implemented, since the AgCl precipitate formed during the titration slowly plugs the frits and decreases the porosity over the course of the titration. A vibrator was used for clearing bubbles from the indicator electrodes, which otherwise interfered with their operation.

With the improvements described here, accuracies of better than $\pm 0.01\%$ were achieved for each SRM. Automated operation assures operator independence and increases the reproducibility of each operation. In addition, the technology for these procedures for high-accuracy coulometric titrations is readily transferred to other laboratories and personnel.

12. The Determination of the Absolute Conductivity of Primary Standards Using a D.C. Method for 1 Demal and 1 Molal KCl Solutions

Y.C. Wu, D. Feng (Guangzhou Research Institute of Non-ferrous Metals, Peoples' Republic of China), W.F. Koch, and L.A. Holland

The electrolytic conductivity values for the 1 D and 1 m standard KCl solutions have been determined absolutely by the d.c. method, from 0 to 50 °C in 5-degree intervals. The novel feature of this method is the cell design which allows the cell constant to be measured independently and mechanically. Hence, the value for conductivity obtained by this method is absolutely determined.

The d.c. method for conductivity is based on the definition of resistance, $R = \rho l/A$, where ρ is the resistivity, $l/\rho = \kappa$, the conductivity; and $l/A = G$, the cell constant. The determination of R is required to use Ohm's law, $V = IR$, where V is the potential and I , the current. Both the current and total resistance must be adjusted to minimize electrolysis and the generation of heat. With today's advanced technology, a 7 or 8 digit DVM can measure a fraction of a μV . In the range of mA and mW, the conductivity of most of the electrolytic solutions can be determined.

There are other advantages and limitations of the d.c. method *viz.*, no lead resistance, which is an important quantity in high conductivity (low resistance) measurement, and the avoidance of the capacitance effect, which is a complicating factor in an a.c. circuit. The limitations are the polarization effect and the requirement of a reversible electrode. The polarization effect may be minimized with a proper design and the reversible electrode may be replaced with a calomel electrode, but in an aqueous media. Overall, we have renewed interest in using the d.c. method for conductivity measurements. Because an accurate a.c. bridge is not commercially available, the d.c. method may serve as an alternative.

The values obtained by the d.c. method for the 1 D and 1 m KCl primary standard solutions agreed with those adopted by the International Organization for Legal Metrology (OIML) at the same temperatures to within $\pm 0.02\%$. We have recommended our values as the primary standards to OIML and to the International Union of Pure and Applied Chemistry (IUPAC).

13. Use of INAA, PGAA, and RNAA to Determine 30 Elements for Certification of an SRM: Tomato Leaves 1573a

D.A. Becker, R.M. Lindstrom, R.R. Greenberg, E.A. Mackey, and K.M. Garrity

Nuclear analytical techniques are used extensively at the NIST in the certification of natural matrix reference materials for major, minor and trace element concentrations. In the renewal botanical reference material Tomato Leaves (SRM 1573a), the three nuclear analytical techniques of instrumental neutron activation analysis (INAA), prompt gamma activation analysis (PGAA), and radiochemical neutron activation analysis (RNAA) have been combined to provide certification data for a total of thirty different elements. In addition, the INAA determinations were made on twelve samples, each approximately 150 mg in size, providing data for the evaluation of homogeneity as well.

For the INAA determinations, the analytical procedure was as follows: six bottles of tomato leaves were randomly selected, with duplicate samples of approximately 150 mg taken for analysis. Primary elemental standards and several SRM control materials were included with the analysis. All samples were irradiated two times, first for 40 seconds at a thermal neutron fluence rate of $2.1 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ followed by counting for short and intermediate half-life products (Al, V, Ca, Mg, Na, K, Mn, Ba, Br), then again for 8 hours in the same facility to determine long

half-life products (Cr, Co, Fe, La, Rb, Sb, Sc, Se, Th, Zn). Data were corrected for differences in neutron fluence, decay times, live time of count, pulse pileup, and weight losses during drying. Corrections were also made where necessary for container blanks and gamma-ray interferences. Concentrations determined ranged from 55 ng/g (Se) to 5.05 % (Ca).

For PGAA, 1-g samples and controls were pressed into pellets, heat-sealed into Teflon FEP envelopes, and irradiated at the NIST thermal PGAA facility for about 13 hours. Compton suppressed spectra of 16384 channels were collected with a pulse height analyzer coupled to a Vax workstation. Titanium foils were irradiated both before and after each sample to monitor the neutron beam. Spectral peaks were integrated with interactive peak analysis computer programs, and multiple peaks were used for each element wherever possible. Elements determined by PGAA were H, B, N, K, Ca, S, Cl, Cd, Sm, and Gd. Corrections were made for neutron fluence rate, dead time, pulse pileup, background, and interfering peaks. Concentrations determined ranged from 0.166 $\mu\text{g/g}$ (Gd) to 5.15% (H).

For RNAA, samples of approximately 250 mg were used from six bottles. Samples, standards and controls were irradiated in the RT-1 pneumatic tube facility for 3 hours. After dissolution with mixed acids, the elements of interest (Sb, As, Cd, Cu, Cr, Se, and Ag) were separated using inorganic ion exchangers and solvent extraction techniques. The RNAA technique is particularly useful to accurately determine extremely low concentrations of trace elements. The seven elements determined here had concentrations ranging from 1.50 to 2000 ng/g.

In conclusion, the three techniques of INAA, PGAA and RNAA have been used to provide certification data for 30 elements in the proposed new SRM 1573a, Tomato Leaves. These elements include major, minor and trace level concentrations. In addition, one technique (INAA) has provided useful homogeneity data on twelve samples at the 150 mg sample size. Indications are that this new reference material, when certified, will provide another excellent botanical SRM for use by analytical laboratories in their quality assurance programs. These analyses represent the most extensive use to date of nuclear analytical techniques in the certification of a trace element SRM at NIST.

14. Prompt Gamma Activation Analysis in the Cold Neutron Research Facility

R.M. Lindstrom and R.L. Paul

There is a need for reliable hydrogen determination at low concentrations. Most common analytical procedures use high-temperature extraction. These methods destroy the sample and are not always accurate. Neutron-capture prompt gamma-ray activation analysis (PGAA) has been used at several laboratories for measurement of hydrogen. The technique is wholly nondestructive, which is important when the analytical sample is to be used for subsequent experiments. It is also specific, which is vital for characterizing reference materials.

The Maryland/NIST thermal PGAA system can measure hydrogen in a variety of materials at moderate concentrations. However, the background spectrum is dominated by the 2223-keV hydrogen capture peak, equivalent to 1 mg of hydrogen. A NIST cold neutron PGAA system was constructed as part of the Cold Neutron Research Facility (CNRF). The hydrogen background in the air is currently 0.07 ± 0.01 c/s, which corresponds to $20 \mu\text{g H}$. About half of this is atmospheric moisture in the beam path, and a quarter from the neutron guide adjacent to the sample. The permanent passive and active shielding and sample support assembly now being assembled is expected to reduce the background to $1 \mu\text{g}$ or below.

The PGAA system has been used for the analysis of hydrogen in a number of samples originating from NIST programs and from academic and industrial laboratories with whom NIST collaborates. Hydrogen was determined for in a $1.0\text{-}\mu\text{m}$ phosphosilicate glass film deposited on a quarter of a 15-cm silicon wafer $670 \mu\text{m}$ thick. In this case the sample was larger than the 20 mm beam; the effective sample mass was about 1 mg. The net hydrogen content in this sample was $0.96 \pm 1.27 \mu\text{g}/\text{cm}^2$, which corresponds to 6 ± 9 wt % of water in the thin glass films.

Numerous specimens of pure and substituted C_{60} fullerenes have been analyzed for hydrogen in support of neutron scattering and chemical experiments. Early samples of C_{60} were found to contain large amounts of contaminant hydrocarbon, so high (0.9 wt %H) as to vitiate the neutron scattering measurements that were planned; repurification gave a satisfactory product with about $600 \mu\text{g}/\text{g}$. With substituted fullerenes, we were often able to measure other elements; for example the H/S molar ratio in a 160-mg sample of $\text{C}_{60}(\text{SO}_4\text{H})_8$ was found to be 1.0 ± 0.1 as expected. We have determined both the major alkali and impurity hydrogen in superconducting K_3C_{60} and its K_6 and Rb_n analogs. In one sample we found 0.9 ± 0.2 mole H per mole Rb, suggesting that this sample may have been exposed to moisture after its synthesis.

We have measured nondestructively the hydrogen concentrations in different locations on two 9×25 cm titanium alloy compressor blades from a turbine engine (one of which had failed), to test the conjecture that embrittlement was due to hydrogen. It was indeed found that one blade contained $200 \mu\text{g}/\text{g}$ or below, while another showed concentrations as high as $700 \mu\text{g}/\text{g}$, especially at the leading edge of the blade.

In agreement with expectations, the use of cold neutrons in the PGAA system has made quantitative measurement of below $10 \mu\text{g}$ of hydrogen routine in suitable sample matrices. Improvement to the analytical system is ongoing. Permanent shielding and gamma collimation now being designed will substantially reduce the background due to the adjacent guide, and a bismuth germinate Compton suppression system being installed should improve the measurability of the single H line in the presence of cascade gamma rays and continuum, as observed in titanium and iron. The sensitivity (counting rate per gram) is expected to improve when a new liquid-hydrogen cold source is installed.

15. Analysis of Boron in Chemical Vapor Deposition (CVD) Diamond Surfaces Using Neutron Depth Profiling

G.P. Lamaze, R.G. Downing, and L. Ilione, A. Badzian, and T. Badzian
(Pennsylvania State Univ.)

There has been a great deal of interest in the use of diamond as a semiconductor device. This interest has been accelerated by the fact that the CVD process simplifies the preparation of diamond films. Performance specifications of Schottky diodes and field effect transistors prepared by the CVD process are similar to those made by the earlier more difficult high temperature, high pressure process. Boron is being used as a dopant in the CVD process by adding small amounts of B_2H_6 to the gas mixture. Boron catalyzes the film growth, decreases the density of stacking faults, and makes the diamond films more resistant to oxidation. It is important to know the depth distribution of boron in the diamond film.

Neutron Depth Profiling (NDP) is a method of near surface analysis for isotopes that undergo neutron-induced positive Q-value charged particle reactions. Because of its large cross section and large Q-value, the $^{10}B(n,\alpha)^7Li$ reaction is one of the best for NDP studies. Depths of about $1\text{ }\mu\text{m}$ are observed with little interference. The technique, which is non-destructive, is a perfect match for the analysis for boron in doped thin diamond films, which are typically about $1\text{ }\mu\text{m}$ thick. Other elements of interest in diamond film technology that can be profiled by NDP are lithium (6Li) and nitrogen (^{14}N).

In this experiment, three homoepitaxial diamond films were grown by microwave plasma assisted chemical vapor deposition and were deposited onto (001) surfaces of natural diamond crystals. The plasma was ignited in a mixture of 1% CH_4 in H_2 . The temperature of the diamond crystals was $900\text{ }^\circ\text{C}$, and the total pressure was 11 kPa (80 Torr). Boron was introduced to the plasma as B_2H_6 . The ratio of B to C atoms in the gas mixture was 1×10^{-2} for sample #1, 5×10^{-3} for #2 and 3×10^{-3} for #3. Raman spectrum of the homoepitaxial diamond film replicated the spectrum of the natural diamond substrate, confirming the quality of the film.

Three boron doped diamond samples and one undoped sample (control) were measured by NDP. Samples #1 and #2 were type IIa diamonds, and Sample #3 was Type Ia. Sample #1, which was very heavily doped and was about $1.6\text{ }\mu\text{m}$ thick, had a boron atom concentration of about $4.2 \times 10^{20}/\text{cm}^3$ that was deposited uniformly with depth. To determine if the boron from sample #1 continued to have a uniform distribution, $0.6\text{ }\mu\text{m}$ was removed from the surface with an oxygen plasma etch, and remeasured by NDP. It was found to be quite uniform. Sample #2, which was not heavily doped and was about $3\text{ }\mu\text{m}$ thick, had about half of that boron concentration near the surface. The concentration decreased as a function of depth by an additional factor of 2 within the first $0.3\text{ }\mu\text{m}$. Sample #3 was lightly doped with boron and grown to a thickness of about $0.5\text{ }\mu\text{m}$. Its larger surface area permitted concentrations as low as $3 \times 10^{18}\text{ at}/\text{cm}^3$ to be measured. The boron distribution was non-uniform with a peak at $0.5\text{ }\mu\text{m}$.

The NDP technique is suitable for measuring boron concentrations and profiles in CVD diamond films. Results for samples #2 and #3 illustrate the sensitivity of NDP to detect changes in boron incorporation during chemical vapor deposition. When flow conditions and diamond growth rate were held constant, boron incorporation was uniform. Through the use of NDP, the effect of different growing and doping conditions can be quantified and correlated with electrical and physical properties.

16. High Resolution Neutron Imaging Using Charge Injection Devices (CIDs)

R.G. Downing, D.F.R. Mildner, and H. Chen (Argonne National Laboratory)

A video radiation detector (VRD) based upon a charge injection device (CID) camera and image processing system has been developed for live-time high resolution imaging of neutron and charged particle fields. The VRD is sensitive to fission fragments, alpha particles, and slow neutrons if a converter is used. Based on commercially available image processing hardware and software, the system is easy to use, inexpensive, and data interpretation is simple. Results are five-dimensional, providing information on x-y position, counts received, energy deposited per count, and time.

The charge injection device (CID) is an imaging sensor used to detect visible, x-ray and UV photons. When an energetic charged particle passes through the capacitance volume of a pixel, it generates electron-hole pairs in the silicon matrix. For example, a 2 MeV alpha particle travels about 8 μm in silicon and can produce 600,000 electron-hole pairs. The electrons are collected and stored within the pixel. The charge collected is proportional to the energy of the charged particle. The CIDs used here have a 755 x 484 pixel format which are digitized with 8-bit charge resolution using an image "grabber" board and a personal computer. The results are processed via custom software and then displayed with a 256-level color scale on a video monitor in live-time.

There are three basic modes for radiography: The first simply retains all pixel intensity information per frame; the second excludes background noise and integrates detected counts into a buffer image; and the third sorts events by pixel intensity. The ability to image visible light, or the sample shadow, is an additional mode of operation, used to register the sample to its radiation map.

The VRD system is essentially 100% efficient for the detection of alpha particles above 4 MeV energy. Emission rates as small as 10^{-5} Bq have been measured. The system allows discrimination between triton, alpha, and fission particles using the rudimentary energy resolution of the pixels. Spatial resolution of less than 12 μm can be achieved by interpolating between pixels. This has been confirmed by correlation of sample position information with transmission electron microscopy data using samples containing alpha sources.

The data provides an x-y distribution map and cumulative particle count for each source. The third dimension represents the number of events occurring at that pixel location. The output is similar to that produced by nuclear emulsions or track-etch detectors, but with some distinct advantages. The processed output is live-time, easily viewed on a monitor without chemical or optical processing, has instant quantitative information, and has the capacity to provide information exceeding the capabilities of most films.

The VRD does not directly detect neutrons, but requires a converter to produce charged particles that are sensed by the CID. For high resolution the converter film is bonded directly to the surface of the CID. An epoxy loaded with ^6LiF is currently being used as the converter film. A neutron detection efficiency for 5 meV neutrons exceeding 2.5% has been achieved.

We have used the device for characterizing neutron focusing components for neutron intensity, determining the focal plane, and analyzing individual elements in the device. Neutron field maps produced by the VRD have been indispensable for the project. The location and size of the focus can be determined much more quickly with the VRD than using a series of photographic films. The VRD has also been used for detecting spontaneous emission of naturally radioactive materials from minerals or contaminants in the analysis of environmental samples.

17. Study of Capillary Optics

D.F.R. Mildner, R.G. Downing, and H. Chen (Argonne National Laboratory)

Materials analysis techniques involving prompt neutron absorption reactions can attain greater accuracy with a focused neutron beam. A prototype neutron lens made of polycapillary glass fibers for focusing neutrons has been constructed at the Kurchatov Institute, Russia. The lens has been evaluated at various neutron ports at the NIST reactor, and at a thermal beam port at a reactor at the Kurchatov Institute. The size and intensity of the neutron beam exiting the lens were recorded with a high resolution Video Radiation Detector (VRD) developed at NIST.

A polychromatic cold neutron beam has been used to obtain a neutron fluence gain of 2.5 in a rectangular aperture which only illuminates a vertical strip at the edge of the lens, encompassing about 200 fibers. With the same aperture located at the center of the lens, the number of illuminated fibers increased to 256 and the gain was 3.6. By evaluating the intensity distribution as a function of the distance from the center of the lens, we estimate the gain to be a factor of 9 for the fully illuminated lens which contains a total number of 721 fibers. We have further evaluated the lens gain at Neutron Guide 7, where the incident beam divergence is much larger (approximately 31.4 mrad). We find that the gain with the lens fully illuminated is 2.7 at this position.

The arrangement of the fibers in the lens is such that the fibers further away from the center (defined by the longitudinal axis) have more severe bending. Therefore, the transmission

efficiency is lower for the fibers near the circumference than those near the center. We have studied this effect by using a series of masking apertures of various diameters at the entrance of the lens. The transmission as a function of the radius of the aperture was compared to the results of computer simulations. The experimental values were consistently lower than the calculated ones by about a factor of 2. We attribute the intensity losses to the surface roughness of the capillaries, as well as to other factors, such as imperfections of the fiber openings, the shape of the capillaries, and, most likely, a misalignment of the fibers. However, from the weak wavelength dependence of the gain at longer wavelengths, we conclude that the discrepancy between the predicted gain and the measured gain is attributed to other factors, such as mechanical imperfection rather than the random roughness of the inner wall of the capillaries.

The lens has been constructed such that the maximum bending allows full transmission of wavelengths above 0.27 nm, assuming perfect collimation of the incident beam. In reality, the wavelength is somewhat higher, since the incident beam always has a certain divergence as well as other gain reduction factors, such as reflectivity and roughness. In fact, both experimental and computer simulation indicate a continuous rise of the gain for wavelength up to 0.31 nm.

With this first lens we have been able to demonstrate neutron focusing to an area of 1 mm² at full width half maximum intensity. The information gained in these experiments, and those in progress, will be used to select new materials from which to construct polycapillary fibers and to design the lens more efficiently. It is predicted that gains approaching a factor of 100, and focal dimensions of a few hundred micrometers, will be achieved during the next couple of years. During the coming year a neutron focusing lens will be tested in conjunction with the prompt gamma activation analysis and neutron depth profiling instruments to take advantage of the high spatial resolution and greater neutron intensity for small samples and sample areas.

18. Consortium on Automated Analytical Laboratory Systems (CAALS)

G.W. Kramer and J.V. Petersen (E.I. DuPont de Nemours Co., Inc.)

The Consortium on Automated Analytical Laboratory Systems (CAALS) was formed to foster the development of automation for analytical chemistry. During the past year, the Consortium had fourteen members. Besides NIST, CAALS membership included ABC Laboratories, Inc.; Applied Analytical Industries, Inc.; BP America; CEM Corporation; the U.S. Environmental Protection Agency (an ex-officio member); Digital Equipment Corporation; the U.S. Department of Energy; E.I. DuPont de Nemours Company, Inc.; Eastman Kodak Company; Hewlett-Packard Company; Occidental Chemical Corporation; The Perkin-Elmer Corporation; and Union Carbide Corporation.

To tap into the expertise, creativity, and vitality of small businesses, the Consortium has created a new program called CAALS Associates. For an annual fee much lower than the cost of a regular CAALS membership, small businesses, trade associations, individuals, and universities

can join the Associates Program and participate in the development of standards and specifications in the Modularity Project.

CAALS activities focus on three projects: A Modularity and Control Communications Standards Project to develop modular instruments and to standardize inter-instrument communications, an Organic Demonstration Project to automate a procedure for the quantitation of diesel fuel residues in soil samples, and an Inorganic Demonstration Project to create a fully automated system for the determination of trace metals in environmental samples. The two demonstration projects serve as test beds for the concepts and ideas coming from the Modularity Project.

The Modularity and Control Communications Standards Project addresses problems of instrument connectivity and interoperability in analytical chemistry by establishing interfacing standards and specifications to make it easier to interconnect individual instruments into complete analytical systems, where raw samples go in and information comes out. CAALS has proposed that instruments or aggregates of instruments be created as Standard Laboratory Modules (SLMs), components whose interactions with the external world are completely specified in the areas of sample interchange, data interchange, and control/status interchange.

CAALS is developing, through quarterly workshops with technical representatives from member organizations, guidelines for creating modular instruments which can be used to build analytical systems by defining the behavior that an SLM exhibits to the outside world. Each SLM has a well defined, public list of operations (command set) that it can perform, including a mandatory core set of commands. Once system operation has begun, each SLM maintains constant communication with its controller and exhibits deterministic behavior by following a stylized operational state diagram. Furthermore, CAALS is standardizing the format of messages and ways that messages are passed between modules. By delineating what messages are communicated (the semantics), and how the messages are sent (the syntax), CAALS is specifying the core of an automated control structure.

In the future, a fully automated analytical system will consist of a group of modules linked to a control computer that takes in a raw sample, prepares it for analysis, carries out any required separations, performs an instrumental determination, maintains a time-stamped log of events, and generates a final report--all without human intervention.

In developing our modularity concept, we find that in some areas, like specifying the communications protocols, we need to select specifications from existing standards that will best serve our needs. Such specifications will contain very few new concepts. We are currently preparing a draft communications specification and hope to have it available for industry comment by next spring.

Other facets of our SLM concept require novel approaches. Since it is not prudent (or in most cases possible) to create standards from untested and unevaluated concepts, CAALS is carrying out research and implementation efforts to assess these ideas. By examining and testing a variety of approaches, CAALS will be able to formulate appropriate and workable specifications for SLMs. This is by necessity a longer term program, but by breaking the problem into manageable portions and clearly identifying the requirements for each portion, CAALS will be able to generate effective specifications.

C. Outputs and Interactions
(Inorganic Analytical Research Division)

1. Publications

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2. Talks

Beary, E.S. and Paulsen, P.J., "Boron Determinations in Botanical Materials Using ICP-MS Isotope Dilution," ASMS Conference, June 6, 1992.

Beary, E.S. and Paulsen, P.J., "Certification of Toxic Metals on Filters, SRM 2676d, Using ICP-MS Isotope Dilution," 1st Conference on ICP-MS, FACSS, Philadelphia, PA, September 1992.

Beck, C.M., "Back to the Future--Classical Analysis at NIST," Department of Chemistry, Juanita College, Huntington, PA, March 31, 1992.

Beck, C.M., "Back to the Future--Classical Analysis at NIST," Department of Chemistry, University of Ohio, Athens, OH, April 4, 1992.

Beck, C.M., "The Preparation and Certification of a Rhodium Standard Reference Material Solution," 24th Annual Conference of the Canadian Mineral Analysts, Val d'Or Quebec, Canada, September 9, 1992.

Becker, D.A., "Determination of Fluorine in Vegetation Reference Materials," American Nuclear Society National Meeting, San Francisco, CA, November 12, 1991. Invited

Becker, D.A., "Determination of Trace Element Impurities in High Temperature Superconductor Starting Materials," American Nuclear Society National Meeting, San Francisco, CA, November 13, 1991. Invited

Becker, D.A., "Problems and Errors in NAA Irradiations," American Nuclear Society National Meeting, San Francisco, CA, November 12, 1991. Invited

Becker, D.A., "Unique Quality Assurance Aspects of INAA for CRM Homogeneity and Certification," 5th International Symposium on Biological and Environmental Reference Materials, Hotel Novotel Am Europaplatz, Aachen, Germany, May 13, 1992.

- Becker, D.A., "Use of INAA, PGAA, and RNAA to Determine 30+ Elements for Certification of An SRM: Tomato Leaves (SRM 1573a)," 2nd International Symposium on Nuclear Analytical Chemistry, University of Toronto, Toronto, Canada, June 3, 1992.
- Becker, D.A., "Neutron Irradiation and Neutron Beam Facilities for NAA, PGAA, and NDP at the NIST Reactor," 2nd International Symposium on Nuclear Analytical Chemistry, University of Toronto, Toronto, Canada, June 4, 1992.
- Becker, D.A., "Instrumental Neutron Activation Analysis of NIST SRM 1573a, Tomato Leaves (Renewal)," American Nuclear Society Annual Meeting, Boston Marriott Copley Place, Boston, MA, June 11, 1992.
- Berezansky, P.A., "MOPSO, A Recommended Alternative to Phosphate-based pH Standards," 203rd American Chemical Society, National Meeting, Sheraton Palace, San Francisco, CA, April 5, 1992.
- Downing, R.G., "The Reactor and Cold Neutron Research Facility at NIST," Korea Research Institute of Standards and Science, Taejon, Korea, October 1, 1991. Invited
- Downing, R.G., "Development and Application of Neutron Depth Profiling Technique and Other Neutron Beam Analytical Applications," Korea Research Institute of Standards and Science, Taejon, Korea, October 4, 1991. Invited
- Downing, R.G., "Neutron Depth Profiling for the Determination of Boron and Oxygen," Seoul National University, Seoul, Korea, October 7, 1991. Invited
- Downing, R.G., "The New Cold Neutron Depth Profiling Instrument at NIST," Korea Advanced Institute of Science and Technology, Taejon, Korea, October 8, 1991. Invited
- Downing, R.G., "The Measurement of Boron at Silicon Wafer Surfaces by Neutron Depth Profiling," Electronics and Telecommunications Research Institute, Taejon, Korea, October 8, 1991. Invited
- Downing, R.G., "Neutron Depth Profiling of Boron Distributions and NDP Instrumentation," Korea Institute of Energy and Resources, Taejon, Korea, October 9, 1991. Invited
- Downing, R.G., "Opportunities in Chemistry at NIST," Tuskegee Institute, Tuskegee, AL, February 27, 1992.
- Downing, R.G., "Elemental Depth Profiling of Materials Using Cold Neutron Beams," Auburn University, Auburn, AL, February 28, 1992. Invited

- Downing, R.G., "Measurement of Boron Distributions in Synthetic Diamonds by Neutron Depth Profiling," Penn State Diamond and Related Materials Consortium Meeting, Pennsylvania State University, Materials Research Laboratory, University Park, PA, March 26, 1992. Invited
- Downing, R.G., "Determination of Boron in Silicon SRM 2137 by Cold Neutron Depth Profiling," 2nd International Symposium on Nuclear Analytical Chemistry, University of Toronto, Toronto, Canada, June 5, 1992. Invited
- Downing, R.G., "Nondestructive Determination of Weight Percent Boron in Dielectric Films," American Nuclear Society Annual Meeting, Boston Marriott Copley Place, Boston, MA, June 11, 1992. Invited
- Downing, R.G., "High Resolution Neutron Imaging Using Charge Transfer Devices," Society of Photo-Optical Instrumentation Engineers' International Symposium on Optical Science and Engineering, San Diego Convention Center, San Diego, CA, July 22, 1992.
- Downing, R.G., "Instrumentation and Application of Neutron Depth Profiling," Chemistry Department, University of Missouri, Columbia, MO, September 11, 1992. Invited
- Downing, R.G., "Analytical Metrology With Neutron Beam Techniques," Chemistry Department, University of Missouri, Rolla, MO, September 14, 1992. Invited
- Downing, R.G., "Neutron Beam Technique for Analytical Chemistry at the NIST Cold Neutron Research Facility," Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, November 2, 1991. Invited
- Downing, R.G., "Neutron Depth Profiling Applications in Semiconductors," Small Accelerator Conference, University of Texas, Denton, TX, November 3, 1992.
- Epstein, M.S., "Taking the Slurry Sampling Method to the Limit . . . Determining Ultra-trace Constituents in High Purity Materials," Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Adams Mark Hotel, Philadelphia, PA, September 21, 1992. Invited
- Epstein, M.S., "Science Investigates Miracles," Eleventh Annual Meeting of the Society for Scientific Exploration, Princeton, NJ, June 13, 1992.
- Fassett, J.D., "The Need for Isotopically Enriched Materials--Analytical Applications," Board on Chemical Sciences and Technology: Workshop on Availability of Isotopically Enriched Materials, National Academy of Sciences, Washington, DC, February 20, 1992.

- Fassett, J.D., "Certification of Standard Reference Materials Using ICP-MS," American Society for Mass Spectrometry, San Francisco Hilton Hotel, San Francisco, CA, November 14, 1991.
- Feng, D., "New Cell for DC Absolute Determination of Electrolytic Conductivity," 204th National Meeting of the American Chemical Society, J.W. Marriott Hotel, Washington, DC, August 23, 1992.
- Greenberg, R.R., "Overview of Research Activities of the NIST Nuclear Methods Group," Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nuclear (IPEN/CNEN), Radiochemistry Division, Caixa Postal 11049, Pinheiros, Sao Paulo, Brazil, March 31, 1992.
- Greenberg, R.R., "Preparation of Standards for Neutron Activation Analysis," Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nuclear (IPEN/CNEN), Radiochemistry Division, Caixa Postal 11049, Pinheiros, Sao Paulo, Brazil, April 1, 1992.
- Greenberg, R.R., "Quality Assurance for Neutron Activation Analysis," Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nuclear (IPEN/CNEN), Radiochemistry Division, Caixa Postal 11049, Pinheiros, Sao Paulo, Brazil, April 2, 1992.
- Greenberg, R.R., "Calculating Detection Limits for Neutron Activation Analysis," Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nuclear (IPEN/CNEN), Division of Radiochemistry, Caixa Postal 11049, Pinheiros, Sao Paulo, Brazil, April 7, 1992.
- Greenberg, R.R., "Dissolution Problems With Botanical Reference Materials," Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nuclear (IPEN/CNEN), Sao Paulo, Brazil, April 7, 1992.
- Greenberg, R.R., "Radiochemical Separations for Neutron Activation Analysis Used at NIST," Instituto de Pesquisas Energeticas e Nucleares (IPEN), Radiochemistry Division, Caixa Postal 11049, Pinheiros, Sao Paulo, Brazil, April 8, 1992.
- Greenberg, R.R., "Nuclear Analytical Research at NIST," Instituto de Engenharia Nuclear, Comissao Nacional de Energia Nuclear (IEN/CNEN), Rio de Janeiro, Brazil, April 9, 1992.
- Greenberg, R.R., "Chelex-100 Pre-Irradiation Separation for Neutron Activation Analysis," Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nuclear

(IPEN/CNEN), Radiochemistry Division, Caixa Postal 11049, Pinheiros, Sao Paulo, Brazil, April 10, 1992.

Greenberg, R.R., "Instrumental Neutron Activation Analysis of a Fresh-Frozen Pilot Whale Liver Quality Assurance Material," 5th International Symposium on Biological & Environmental Reference Materials, Novotel, Am Europaplatz, Germany, May 11, 1992.

Greenberg, R.R., "Accuracy in Neutron Activation Analysis," Technical University, IRI, Delft, The Netherlands, May 18, 1992. Invited

Greenberg, R.R., "Nuclear Analytical Techniques Used for the Certification of Elemental Concentrations in NIST Standard Reference Materials," 7th Canadian Chemical Conference and Exhibition, Convention Centre, Edmonton, Canada, June 1, 1992.

Greenberg, R.R., "Accuracy in Standards Preparation for Neutron Activation Analysis," 2nd International Symposium on Nuclear Analytical Chemistry, University of Toronto, Toronto, Canada, June 3, 1992.

Greenberg, R.R., "Application of Radiochemical Neutron Activation Analysis for the Certification of Elemental Concentrations in NIST Standard Reference Materials," 3rd International Conference on Nuclear and Radiochemistry, Vienna, Austria, September 8, 1992.

Kelly, W.R., "Meteorites," Adventure in Science, Gaithersburg, MD, February 29, 1992.

Kelly, W.R., Murphy, K.E., and Paulsen, P.J., "Determination of Sulfur in Fossil Fuels by Isotope Dilution - Thermal Ionization Mass spectrometry," ASMS Conference, June 1992.

Kelly, W.R., "Tracing Air Pollution With Enriched Stable Isotopes as Aerosol Tracer: I. Simultaneous Determination of ^{149}SM and ^{150}SM in Particulates by Thermal Ionization Mass Spectrometry," 204th ACS National Meeting, Washington, DC, August 26, 1992.

Koch, W.F., "Standards for Conductivity and Salinity," David Taylor Research Center, Naval Warfare Assessment Center, Annapolis, MD, June 9, 1992.

Koch, W.F., "Conductivity Detection in Ion Chromatography," Bureau of Alcohol, Tobacco, and Firearms, Rockville, MD, 1992.

Kramer, W.G., "Helping Laboratory Automation Live Up to Its Promise," International Symposium on Laboratory Robotics and Automation, Boston, MA, October 22, 1991.

Kramer, W.G., "The Consortium on Automated Analytical Laboratory Systems," University of Maryland, Department of Chemistry, College Park, MD, November 1, 1991.

- Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems," 3M Corporation, St. Paul, MN, November 21, 1991.
- Kramer, G.W., "An Overview of The Consortium on Automated Analytical Laboratory Systems," E.I. DuPont de Nemours, Inc., Wilmington, DE, December 12, 1991.
- Kramer, G.W., "Environmental Laboratory Productivity: Meeting Today's Challenge," Analytical Products Group, Hewlett Packard, Palo Alto, CA, February 2, 1992.
- Kramer, G.W., "Standards for Scientific Instrument Interfacing a Technological Necessity," 1st International Symposium on Laboratory Robotics and Artificial Intelligence Applied to Analytical Chemistry," Montreux, Switzerland, February 26, 1992.
- Kramer, G.W., "Modularity and Communications for Analytical Chemistry Instrumentations," PITTCON, New Orleans Convention Center, New Orleans, LA, March 9, 1992.
- Kramer, G.W., "Recent Progress of The Consortium on Automated Analytical Laboratory Systems," Digital Equipment Corporation, Marlboro, MA, June 1, 1992.
- Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems (CAALS)," ASTM Workshop on Standards Impacting LIMS at the 6th International LIMS Conference, Pittsburgh, PA, June 8, 1992.
- Kramer, G.W., "Standard Modules as Building Blocks for Laboratory Automation," American Chemical Society, Moscone Center/Hilton Tower, San Francisco, CA, 1992.
- Kramer, G.W., "Scientific Laboratory Automation System Standards: Industry-wide Programs and Projects," LAPQUIP, Information Science Services, Inc., Philadelphia Civic Center, Philadelphia, PA, October 2, 1991.
- Kramer, G.W., "A Standard Interface for Laboratory Equipment--What Do We Really Want," FACSS, Disneyland Hotel and Convention Center, Anaheim, CA, October 10, 1991.
- Kramer, W.G., "Scientific Laboratory Automation System Standards," Perkin-Elmer, Norwalk, CT, November 6, 1991.
- Lamaze, G.P., "Cold Neutron Source: Detection of Hydrogen and Boron," Workshop on Characterizing CVD Diamond, Gaithersburg, MD, February 27, 1992. Invited
- Lamaze, G.P., "Nondestructive Boron and Lithium Profiling in Diamond Films Using Neutron Depth Profiling," Penn State Diamond and Related Materials Consortium Meeting, University Park, PA, March 26, 1992. Invited

Lamaze, G.P., "Analysis of Boron in CVD Diamond Surfaces Using Neutron Depth Profiling," 6th International Conference on Solid Films and Surfaces, Paris, France, June 29, 1992.

Lamaze, G.P., "Mass Assay and Uniformity Tests of Boron Targets by Neutron Beam Methods," 16th World Conference of the International Nuclear Target Development Society, Legnaro, Italy, September 21-25, 1992.

Lankosz, M., Holynska, B., Pella, P.A., "Research in the Quantitative Analysis of Individual Particles by X-Ray Microfluorescence Spectrometry," 41st Annual Denver X-Ray Conference, Colorado Springs, CO, August 5, 1992.

Lin, Z.C., Ondov, J.M., and Kelly, W.R., "Enriched Isotopes as Aerosol Tracer: II. Definitive Apportionment of Coal-Fired Power Plant, Diesel, and Oil Furnace Emissions," 204th ACS National Meeting, Washington, DC, August 26, 1992.

Lin, Z.C., Ondov, J.M., and Kelly, W.R., "Enriched Rare-Earth Isotopes as Definitive Tracers of Aerosol from High-Temperature Combustion Sources," European Aerosol Conference, Oxford, England, September 6-11, 1992.

Lindstrom, R.M., "Research Activities with Prompt-Gamma and Cold Neutron Beam Facilities at the Inorganic Analytical Research Division of the NIST," Dipartimento di Chimica Generale, University of Pavia, Italy, October 1, 1991. Invited

Lindstrom, R.M., "Control of High Count Rate and Decay Effects," American Nuclear Society Winter Meeting, San Francisco, CA, November 12, 1991. Invited

Lindstrom, R.M., "Determination of Iodine and Iodine-129 in Several New Botanical SRMs by NAA," American Nuclear Society Winter Meeting, San Francisco, CA, November 12, 1991. Invited

Lindstrom, R.M., "Analytical Chemistry with Cold Neutron Beams at NIST," Department of Chemistry, Japan Atomic Energy Research Institute, Tokai, Japan, March 2, 1992. Invited

Lindstrom, R.M., "High-Sensitivity Gamma Counting at NIST," National Institute of Radiological Sciences, Nakaminato, Japan, March 6, 1992. Invited

Lindstrom, R.M., "Utility Software for Gamma Spectrometry," Nuclear Data Users Group, Cranberra Instruments, Bethesda Marriott, Bethesda, MD, May 1, 1992.

Lindstrom, R.M., "High Sensitivity Gamma Counting," Nuclear Data Users Group, Canberra Instruments, Bethesda Marriott, Bethesda, MD, May 1, 1992.

- Lindstrom, R.M., "Measuring Hydrogen by Prompt-Gamma Activation Analysis," 2nd International Symposium on Nuclear Analytical Chemistry, University of Toronto, Toronto, Ontario, Canada, June 5, 1992. Invited
- Mackey, E.A., "Accuracy in Neutron Capture Prompt Gamma-Ray Activation Analysis of Hydrogenous Materials," American Nuclear Society Winter Meeting, San Francisco, CA, November 12, 1991.
- Mackey, E.A., "Determination of Tin in Human Liver Tissue Using RNAA," 3rd International Conference on Nuclear and Radiochemistry, Vienna, Austria, September 10, 1992.
- Messman, J.D., Smith, M.V., Winchester, N., "Considerations for Certification Renewal of a Liquid Wavelength Standard Reference Material for Ultraviolet/Visible Spectrophotometry," 34th Rocky Mountain Conference on Analytical Chemistry, Radisson Hotel, Denver, CO, August 4, 1992.
- Mildner, D.F.R., "Focusing Neutrons Using Capillary Optics," NIST Chemical Science and Technology Laboratory Annual Review, February 11, 1992.
- Mildner, D.F.R., "Focusing Neutrons Using Capillary Optics," European Spallation Source Instrumentation and Techniques Expert Meeting, Abingdon, England, February 26, 1992.
- Mildner, D.F.R., "Focusing Neutrons Using Capillary Optics," Demokritos National Research Center for Physical Sciences, Athens, Greece, March 19, 1992.
- Mildner, D.F.R., "Characterizing a Neutron Lens: Study of Capillary Optics," Conference on Neutron Optical Devices and Applications, SPIE, International Symposium on Optical Applied Science and Engineering, San Diego, CA, July 24, 1992.
- Mildner, D.F.R., "Promise of Thin Silicon Wafer Microguides for Future Optical Elements," Society of Photo-Optical Instrumentation Engineers' International Symposium on Optical Science and Engineering, San Diego Convention Center, San Diego, CA, July 24, 1992.
- Mildner, D.F.R., "Developing a Focused Neutron Probe for Materials Analysis," 26th Annual Meeting of Microbeam Analysis Society, Hynes Convention Center, Boston, MA, August 20, 1992. Invited
- Norman, B.R., "Iodine Determination in Biological and Environmental Materials," 5th International Symposium on Biological and Environmental Reference Materials, Aachen, Germany, May 12, 1992.

- Paul, R.L., "Cold Neutron Prompt Gamma Activation Analysis at NIST - A Progress Report," 2nd International Symposium on Nuclear Analytical Chemistry, University of Toronto, Toronto, Canada, June 5, 1992.
- Paulsen, P.J. and Beary, E.S., "ICP-MS Isotope Dilution Analysis for Ten Elements in Wear Metals in Oil SRMs," FACSS, "Disneyland Hotel and Convention Center, Anaheim, CA, October 9, 1991.
- Paulsen, P.J. and Beary, E.S., "ID-ICP-MS Certification of Toxic Metals on Filters," Durham Conference on ICP-MS, Durham, United Kingdom, September 15, 1992. Invited
- Pella, P.A., Steel, E.B., Kelly, W.R., and Murphy, K.E., "Zinc Sulfide Standard Reference Thin Film for X-Ray Spectrometry," 41st Annual Denver X-Ray Conference, Colorado Springs, CO, August 5, 1992.
- Pella, P.A. and Lankoz M., "Quantitative X-ray Microfluorescence Analysis of Small Areas and Individual Particles," Electron Microscopy Society of America, Convention Center, Boston, MA, August 20, 1992.
- Pella, P.A., McKnight, M., Murphy, K.E., Wood, L.J., Vocke, R.D., Byrd, E., Watters, R.L., Kane, J.S., Lagergren, E.S., Schiller, S.B., and Marlow, A.F., "NIST SRM 2579 Lead Paint Films for Portable X-ray Fluorescence Analyzers," 204th American Chemical Society National Meeting, Washington Convention Center, Washington, DC, August 25, 1992.
- Petersen, J.V., "NIST CAALS: The Application of Modularity to Microwave - Assisted Sample Dissolution," PITTCO, New Orleans Convention Center, New Orleans, LA, March 9, 1992.
- Pratt, K.W., "Systematic Errors in Coulometric Titrations of Strong Acids," 4th European Conference on Electroanalysis, Conference Center de Leeuwenhorst, Noordwijkerhout (Leiden), Netherlands, June 2, 1992.
- Pratt, K.W., "Automated High-Precision Coulometry," 4th European Conference on Electroanalysis, Conference Center de Leeuwenhorst, Noordwijkerhout (Leiden), Netherlands, June 3, 1992.
- Pratt, K.W., "Evaluation of Systematic Errors in Coulometric Acidimetry," 204th National Meeting of the American Chemical Society, J.W. Marriott Hotel, Washington, DC, August 23, 1992.
- Salit, M.L., "NIST CAALS: Strategies for Grafting Modularity onto Existing Instruments," PITTCO, New Orleans Convention Center, New Orleans, LA, March 9, 1992.

- Salit, M.L., "Subtractive Cancellation of Multiplicative Noise Using the Complementary Output Channels of a UV/Visible Fourier Transform Spectrometer," High Resolution Fourier Transform Spectroscopy Optical Society of America, University of Colorado, Boulder, CO, August 29, 1992.
- Travis, J.C., "Dual Channel Noise Reduction in Ultra-Violet Fourier Transform Spectrometry," Spectroscopy Society of Canada, Trent University Conference Center, Peterborough, Ontario, Canada, August 8, 1992.
- Travis, J.C., "Application of Fourier Transform Optical Spectrometry to the Preparation of a Spectral Atlas for Inductively-Coupled Plasma Optical Emission Spectrometry," 2nd Topical Meeting on High Resolution Fourier Transform Spectrometry Optical Society of America, College Inn Conference Center, University of Colorado, Boulder, CO, August 27, 1992.
- Turk, G.C., "Spatially Selective Detection of Anomalous Contributions to Laser-Enhanced Ionization in Flames," 6th International Symposium on Resonance Ionization Spectroscopy and Its Applications, Eldorado Hotel, Santa Fe, New Mexico, May 26, 1992.
- Vocke, R.D., Poster Session: 1st National Conference on Laboratory Issues in Childhood Lead Poisoning Prevention, Columbia, MD, October 31-November 2, 1991.
- Vocke, R.D., "Mathematical Models for the Petrogenesis of the Harzburger Gabbro, Germany," Carnegie Institution of Washington, Washington, D.C., April 1, 1992. Invited
- Vocke, R.D., Murphy, K.E., Paulsen, P.J., "The Accurate Analysis of Lead in Blood - Standards and Methods Development," 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Vocke, R.D., "Isotopic Reference Materials--Absolute or Otherwise," Application of Isotope Systems to Geological Problems Workshop, U.S. Geological Survey, National Center, Reston, VA, September 14, 1992.
- Winchester, M.R., "Fourier Transform Spectroscopy in the Ultraviolet/Visible Spectral Range: Comparison of Noise Characteristics Using An Inductively Coupled Plasma and a Glow Discharge Source," FACSS, Disneyland Hotel and Convention Center, Anaheim, CA, October 11, 1991.
- Winchester, M.R., "Studies of Noise and Its Analytical Implications in Fourier Transform Spectroscopy in the Ultraviolet Visible Spectral Range Using a Glow Discharge Source," PITTCO, New Orleans Convention Center, New Orleans, LA, March 10, 1992.

Winchester, M.R., "The Glow Discharge as an Analytical Emission Source for Fourier Transform Spectroscopy," 19th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Adams Mark Hotel, Philadelphia, PA, September 23, 1992.

Wu, Y.C., "The Research on the Standards of pH and of Electrolytic Conductivities," National Office of Measures, Budapest, Hungary, November 17, 1991.

Wu, Y.C., Berezansky, P.A., Daming, F., and Koch, W.F., "Dissociation Constant of N,N-bis (2-Hydroxyethyl) 2-Aminoethanesulfonic Acid and pH of Its Buffer Solutions," 204th National Meeting of the American Chemical Society, Washington, D.C., August 23, 1992.

Wythoff, B.J., "Identification of Organic Functional Groups Using Vapor Phase Infrared Spectra and Artificial Neural Networks: Toward Optimal Orthogonal Bases for Arbitrary Mathematical Functions," Department of Chemistry, University of British Columbia, Vancouver, B.C., June 15, 1992.

Wythoff, B.J. and Stein, S.E., "Identification of Organic Functional Groups Using Vapor Phase Infrared Spectra and Artificial Neural Networks," FACSS Conference, Philadelphia, PA, September 24, 1992. Invited

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Advancement of the Quality of Clinical Laboratory Work in the United States, W.F. Koch
College of American Pathologists (CRADA)

Analysis of Semi-conductor Materials by Neutron Beam Techniques, R.G. Downing
Intel Corporation (CRADA)

Biomedical Applications of Analytical Spectroscopy, J.D. Fassett
Eastern Analytical, Inc. (CRADA)

Consortium for Automated Analytical Laboratory System, G.W. Kramer
ABC Laboratories, Inc. (CRADA)
Applied Analytical Industries, Inc. (CRADA)
BP America (CRADA)
CEM Corporation (CRADA)
Department of Energy and the National Laboratories (CRADA)
Digital Equipment Corporation (CRADA)
E.I. duPont de Nemours Company, Inc. (CRADA)
Eastman Kodak Company (CRADA)

Environmental Protection Agency (CRADA)
Hewlett-Packard Company (CRADA)
Occidental Chemical Corporation (CRADA)
The Perkin-Elmer Corporation (CRADA)
Union Carbide Corporation (CRADA)

Effects of Radiation on the Performance of Charge Injection Devices, R.G. Downing
CID Technologies, Inc. (CRADA)

Investigation of Neutron Focusing Using Capillary Optics, R.G. Downing
X-Ray Optical Systems, Inc. (CRADA)

Surface Properties of Refractory Transition Metal Carbides, R.G. Downing
Linfield College (CRADA)

4. Patent Awards and Applications

Kingston, H.M. and Siriraks, A., "System for Detecting Transition and Rare Earth Elements in a Maxtrix," (Awarded June 1992, 88-038)

5. SRM Activities

39j benzoic acid	136e potassium dichromate
458 Be-Cu Alloys	1400 bone ash
459 Be-Cu Alloys	1486 bone meal
460 Be-Cu Alloys	1515 apple leaves
918a potassium chloride, clin.	1547 peach leaves
927b bovine serum albumin	1570a spinach leaves
929 magnesium gluconate	1573a tomato leaves
930d glass filters, visible	1579 lead in paint
931e liquid filters, UV/vis	1633b coal fly ash
942a lithium carbonate	1930 glass filters, extended
955a lead in blood, level I	2031 metal-on-quartz filters
955a lead in blood, level II	2108 spectrometric solution
955a lead in blood, level III	2109 spectrometric solution
955a lead in blood, level IV	2183 MOPSO
999a potassium chloride	2184 MOPSO sodium salt
1037 natural water	2579 lead paint film
1084a wear metals in oil	2676d toxic metals on filters
1085a wear metals in oil	2683b coal
1249 alloy	2684b coal
	2694a simulated rainwater

2695 fluoride in vegetation	3161 spectrometric solution
2709 soil	3162 spectrometric solution
2710 soil	3163 spectrometric solution
2711 soil	3149 spectrometric solution
2724 diesel fuel oil	3150 spectrometric solution
3101 spectrometric solution	3151 spectrometric solution
3102 spectrometric solution	3152 spectrometric solution
3103 spectrometric solution	3153 spectrometric solution
3104 spectrometric solution	3154 spectrometric solution
3105 spectrometric solution	3155 spectrometric solution
3106 spectrometric solution	3164 spectrometric solution
3107 spectrometric solution	3165 spectrometric solution
3108 spectrometric solution	3166 spectrometric solution
3109 spectrometric solution	3167 spectrometric solution
3110 spectrometric solution	3168 spectrometric solution
3112 spectrometric solution	3169 spectrometric solution
3113 spectrometric solution	3171a spectrometric solution
3114 spectrometric solution	3172 spectrometric solution
3115 spectrometric solution	3182 anion solution, chloride
3116 spectrometric solution	3184 anion solution, bromide
3117 spectrometric solution	3185 anion solution, nitrate
3119 spectrometric solution	3186 anion solution, phosphate
3121 spectrometric solution	3190 electrolytic conductivity
3123 spectrometric solution	3191 electrolytic conductivity
3126 spectrometric solution	3192 electrolytic conductivity
3128 spectrometric solution	3193 electrolytic conductivity
3129 spectrometric solution	3194 electrolytic conductivity
3130 spectrometric solution	3195 electrolytic conductivity
3131 spectrometric solution	3196 electrolytic conductivity
3132 spectrometric solution	8400 sewage sludge
3133 spectrometric solution	
3134 spectrometric solution	
3135 spectrometric solution	
3136 spectrometric solution	
3138 spectrometric solution	
3139 spectrometric solution	
3140 spectrometric solution	
3141 spectrometric solution	
3143 spectrometric solution	
3148 spectrometric solution	
3158 spectrometric solution	
3159 spectrometric solution	
3160 spectrometric solution	

Analytical services have been provided for the following:

Building and Fire Research Laboratory, NIST
Chemical Kinetics and Thermodynamics Division, NIST
IBM East Fishkill Facility, Hopewell Junction, NY
Office of Information Services, NIST
Organic Analytical Research Division, NIST
Standard Reference Materials Program, NIST
Surface and Microanalysis Science Division, NIST
U.S. Geological Survey, Reston, VA

6. SRD Activities

None

7. Calibrations

Special tests (transmittance filter standards) have been provided for the following:

Abbott Chemicals, Inc.	Cetus Corporation
Abbott Diagnostics Division	Chelsea Laboratories, Inc.
Abbott Hospitals, Inc.	Chiron (Cetus) Corporation
Abbott Laboratories	Corion Corporation
Abbott Puerto Rico Operations	Coulter Diagnostics
Albarracin, Ivan V.	Dayton Brown
Allied Signal, Inc.	Dow Chemical Company
Amgen, Inc.	E.I. duPont De Nemours & Company, Inc.
Bacharach, Inc.	E.M. Diagnostic Systems, Inc.
Barr Associates, Inc.	Eastman Kodak Co.
Bausch & Lomb	Eastman Kodak Company
Baxter Diagnostics-Puerto Rico	Ethicon, Inc.
Baxter Healthcare Corporation	Florida Power Corporation
Beckman Instruments	General Dynamics
Ben Venue Laboratories, Inc.	Genetech, Inc.
Bioanalytical Instruments, Inc.	Georgia Power Company
Burroughs Wellcome Company	Helena Laboratories
CIBA Corning Diagnostics	Hitachi Instruments, Inc.
CIBA-GEIGY Corporation	Hoechst Celanese
Cal Check	Honeywell, Inc.
California Chili & Spice	ICI Pharmaceutical Group
Centocor, Inc.	Jasco, Inc.
Central Pharmaceutical, Inc.	Johnson & Johnson, Inc.

Martec Pharmaceutical, Inc.
Mayo Foundation
Merck & Company
Merck, Sharp and Dohme
Miles, Inc.
Miles, Inc.
Milton Roy
National Standards of Puerto Rico
New Hampshire Yankee
Nordion International, Inc.
Nutra Sweet
Olin Corporation
Organon Teknika Corporation
Ortho Pharmaceutical Corporation
Oxford Labware (Sherwood Med)
Pacific Optical
Parke-Davis
Pepsi-Cola Company
Perkin Elmer Corporation
Perkin-Elmer AG
Pharmaceutical Research Institute
Presbyterian University Hospital
Pyrometer Associates, Inc.
Roche Products, Inc.

Searle
Shimadzu Scientific Instrument
Sigma Chemical Company
Sonneborn Division
South Bend Medical Foundation
Southern California Edison
St. Vincent Charity Hospital
Sterling Drug, Inc.
Sterling Products International
Stolle Research & Development
Syva Company
TVA-Chattanooga Distribution Center
Technicon
Tennessee Valley Authority
Texas Eastman Company
The UpJohn Company
UOP, Inc.
USCI
Union Carbide Corporation
Varian
Varian Canada, Inc.
Zimmer, Inc.

8. Committee Assignments

E.S. Beary

EEO Representative, CSTL
SNM Custodian, CSTL

C.M. Beck II

ASTM, E1 Chemical Analysis of Metals, Ores, and Related Materials
ASTM, E1.02 Ores, Concentrates and Related Metallurgical Materials

D.A. Becker

ANS, SC.16 Isotopes and Radiation
ANS, WG.01 Trace Element Analysis Committee
ANS, C004 Biology and Medicine
ANS, WG.01 Activation Analysis
ANS, C006 Standards Steering Committee
ASTM, E10 Nuclear Technology and Applications

ASTM, E10.05 Nuclear Radiation Metrology
ASTM, E10.05.12 Nuclear Methods of Chemical Analysis (Chairman)
ASTM, WG.08 Nuclear Environmental Metrology
ASTM, WG.10 Neutron Metrology

D.S. Braverman

Society of Applied Spectroscopy, Baltimore/Washington Section (Treasurer)

J.R. DeVoe

EPA Special Interagency Task Subgroup on Method Development and Standards for Lead Analysis (Chairman)

R.G. Downing

ASTM, F1 Electronics
ASTM, F1.WG.11 Alpha Particle Induced Soft Errors
ASTM, E10 Nuclear Technology and Applications
ASTM, E10.05 Nuclear Radiation Metrology
ASTM, E10.05.12 Nuclear Methods of Chemical Analysis
CSTL Colloquia Committee

M.S. Epstein

Tellers Committee, Society for Applied Spectroscopy
Board of Directors, National Capital Area Skeptics
EPA Working Committee on Lead Based Paint Good Lab Practices Guide
Program Committee, Society for Scientific Exploration Annual Meeting
Judge, Montgomery Area Science Fair
Mentor, Arlington County Schools PRIME (Profession-Related Intern-Mentor Experience Program)

R.F. Fleming

ASTM, E10 Nuclear Technology and Applications
ASTM, E10.05 Nuclear Radiation Metrology
ASTM, E10.07 Radiation Effects on Materials
ASTM, E10.07.04 Radiation Metrology for Food Processing

R.R. Greenberg

ASTM, E10 Nuclear Technology and Applications
ASTM, E10.05 Nuclear Radiation Metrology
ANS, Trace Analysis Committee, Division of Biology and Medicine
ANS, Executive Board, Division of Biology and Medicine
NIST Radiation Safety Committee

W.R. Kelly

NIST Colloquium Committee (Chairman)

W.F. Koch

NCCLS, Board of Directors

NCCLS, National Committee for Clinical Laboratory Standards

ASTM, D-19 Water

ASTM, D-22 Sampling and Analysis of Atmospheres

ASTM, D-22.06 Acid Deposition

ASTM, D-22.06.03 in Atmospheric Deposition pH

ASTM, D-22.02 General Specifications and Technical Resources

AWWA, C002 Standards Methods

ASTM, D-19.05 Inorganic Constituents in Water

IUPAC, 005 Analytical Chemistry Division

IUPAC, C.05.5 Electroanalytical Chemistry

G.W. Kramer

ASTM, E31 Computerized Systems

ASTM, E31.40 Laboratory Information Management Systems

ASTM, E49 Computerization of Material Property Data

ASTM, E49.52 Experimental Data Interchange

NIST Electronics Storeroom Committee

G.P. Lamaze

ASTM, E10 Nuclear Technology and Applications

ASTM, E10.95 Long Range Planning

ASTM, E10.05 Nuclear Radiation Metrology

ASTM, E10.94 Membership Subcommittee

J.K. Langland

NIST Electronics Storeroom Committee (Chairman)

R.M. Lindstrom

NIST Radiation Safety Committee

NIST Reactor Safety Evaluation Committee

J.D. Messman

SAS Audit Committee (Chairman)

SAS Tellers Committee

ASTM, E013 Molecular Spectroscopy

ASTM, SC.01 UV/Vis Spectrophotometry

J.R. Moody

ASTM, D-19 Water
ASTM, D-19.05 Inorganic Constituents in Water
ACS, C002 Analytical Reagents
IUPAC, 002 Inorganic Chemistry Division
IUPAC, SC.02 Isotopic Specific Measurements as References
IUPAC, C.02.01 Atomic Weights
IUPAC Sub-commission on Isotopic Abundance Measurements (Chairman)
Society for Applied Spectroscopy, Baltimore/Baltimore Section (Chairman)
CSTL Quality Assurance Committee

P.A. Pella

ASTM, E.01 Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, SC.22 Statistics and Quality Control

K.W. Pratt

NIST Research Information Center, Division 834 Subject Specialist
Inorganic Analytical Research Division Seminar Committee
Inorganic Analytical Research Division High Purity Reagents Committee

M.V. Smith

ASTM, E013 Molecular Spectroscopy
ASTM, SC.01 Ultraviolet and Visible Spectroscopy

T.W. Vetter

ASTM, E01 Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, SC.01 Irons, Steels, and Ferroalloys
ASTM, SC.02 Ores, Concentrates, and Related Metallurgical Materials
ASTM, WG.01 ISO TAG on Concentrates
ASTM, SC.21 Reference Materials and Liaison with S17
ASTM, SC.23 Terminology
ASTM, SC.24 Editorial and Publications

R.D. Vocke

Division 834 Lunch Bunch Committee
Division 834 Colloquium Committee

R.L. Watters, Jr.

Federation of Analytical Chemistry & Spectrometry Society Governing Board
ASTM, E01 Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, 1.01 Iron, Steel, and Ferroalloys
ASTM, 1.20 Fundamental Practices
ASTM, 1.22 Statistics and Quality Control (Vice Chairman)

Yung C.W.

ASTM, D19 Water
ASTM, D19.05 Inorganic Constituents in Water
ASTM, SC.09 Saline and Brackish Waters

9. Editorships

M.S. Epstein

Journal of Analytical Atomic Spectroscopy (Editorial Advisory Board)
Special Issue of Spectrochimica Acta B on Reference Materials and Reference Methods
(Guest Editor)
Journal of Scientific Exploration (Column Editor)

G.W. Kramer

Laboratory Robotics and Automation (Editorial Advisory Board)
Intelligent Instruments and Computers (Executive Editor)
American Chemical Society, Computer Buyer's Guide

P.A. Pella

X-Ray Spectrometry (Advisory Board)

J.C. Travis

Spectrochimica Acta B (Editorial Advisory Board)

G.C. Turk

Atomic Spectrometry Updates (Editorial Board)

10. Seminars

October 4, 1991

Mikhail Bolshov, Institute of Spectroscopy, Troitsk, U.S.S.R., "The Problem of Reference Materials for Ultrasensitive Analysis by Laser-Excited Atomic Fluorescence Spectrometry." (Division Sponsor: G.C. Turk)

October 4, 1991

Jose A. C., Broekaert, Department of Chemistry, University of Dortmund, Dortmund 50, GERMANY, "Atomic Spectrometric Methods for the Analysis of Ceramics." (Division Sponsor: J.C. Travis)

October 21, 1991

Steve Lehotay, Department of Chemistry, University of Florida, Gainesville, FL 32611-2046, "A Different Approach to Single-Molecule Detection Using Laser-Induced Fluorescence." (Division Sponsor: M.S. Epstein)

October 24, 1991

William Windig, Eastman Kodak Company, Kodak Park, Building 49, Rochester, New York 14652-3712, "Self-Modeling Mixture Analysis." (Division Sponsor: B.J. Wythoff)

December 11, 1991

Walter M. Gibson, Director, Center for X-Ray Optics, State University of New York, Albany, NY, "A New X-ray and Neutron Optics With Wide Angular Aperture and Broad Energy Band Width." (Division Sponsor: D.F.R. Mildner)

December 11, 1991

Muradin A. Kumakhov, Nalchek University, Institute of Roentgen Optical Systems World Lab, Moscow, Russia, "A New X-ray and Neutron Optics With Wide Angular Aperture and Broad Energy Band Width." (Division Sponsor: D.F.R. Mildner)

December 17, 1991

Jean A. Pauwels, Sample Preparations Group, Central Bureau for Nuclear Measurements, Geel, Belgium, "Preparation of Biological and Environmental Reference Materials at CBNM." (Division Sponsor: G.P. Lamaze)

March 20, 1992

Phillip T. Taylor, Joint Research Center, Central Bureau for Nuclear Measurements, Geel, Belgium, "The Atomic Weight of Iron." (Division Sponsor: R.D. Vocke)

April 15, 1992

Raymond E. Dessy, Virginia Polytechnic Institute & State University, Blacksburg, VA, "Getting I.T. All Together Automating Entire Technical Centers." (Division Sponsor: G.W. Kramer)

April 22, 1992

Adrian P. Wade, Laboratory for Automated Chemical Analysis, University of British Columbia, Vancouver, British Columbia, "Developments in Automated Flow Injection Analysis." (Division Sponsor: B.J. Wythoff)

June 24, 1992

Vance Kirshner, Labware, Inc., Wilmington, DE, "LabStation." (Division Sponsor: G.W. Kramer)

June 24, 1992

James Barantz, Digital Equipment Corporation, Marlboro, MA, "Manufacturing Messaging System Standards." (Division Sponsor: G.W. Kramer)

August 17, 1992

Emanuel Svucman, University of Veterinary Medicine & Pharmaceuticals, Department of Biochemistry and Biophysics, Brno, Czechoslovakia, "Importance of the Sample Preparation Technique for the Electrochemical Trace Element Analysis." (Division Sponsor: K.W. Pratt)

September 9, 1992

Steven Ray, NIST, Factory Automation Systems Division, "The NIST Process Planning Testbed." (Division Sponsor: G.W. Kramer)

September 9, 1992

M. Kate Senehi, NIST, Factory Automation Systems Division, "Manufacturing Systems Integration." (Division Sponsor: G.W. Kramer)

September 14, 1992

Stephen Long, "ICP-MS: A Flexible Tool for the Determination of Trace Elements." (Division Sponsor: W.F. Koch)

September 21, 1992

Chitra J. Amarsiriwardena, University of Massachusetts, Cambridge, MA, "Applications of Inductively Coupled Plasma Mass Spectrometry to Biomedical Studies." (Division Sponsor: W.F. Koch)

11. Conferences/Workshops Sponsored/Co-Sponsored

October 30, 1991

EPA Working Group on Quality Assurance and Reference Materials, National Institute of Standards and Technology, Gaithersburg, Maryland

November 7-8, 1991

NCCLS 1992 Area Committee Planning and Board of Directors Meeting, NCCLS and the National Institute of Standards and Technology, Gaithersburg, Maryland

November 13-15, 1991

CAALS Oversight Board Meeting, National Institute of Standards and Technology, Gaithersburg, Maryland

November 27, 1991

High Purity Metals, National Institute of Standards and Technology, Gaithersburg, Maryland

December 13, 1991

EPA Interagency Task Group on Methods & Standards of Lead-based Paint, National Institute of Standards and Technology, Gaithersburg, Maryland

April 1-3, 1992

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

May 20-21, 1992

CAALS Oversight Board, National Institute of Standards and Technology, Gaithersburg, Maryland

June 24-26, 1992

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

September 9-11, 1992

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

V. Organic Analytical Research Division (835)

Willie E. May, Chief

A. Division Overview

The Organic Analytical Research Division is the National source for measurement science, reference materials/standards and related information pertaining to the characterization and quantitative analysis of organic compounds both pure and in complex matrices, and the chemical characterization of gaseous mixtures.

The Division has a staff of approximately 50 scientists with research activities being carried out in four groups. *The Analytical Sensors and Automation Group* researches and implements new rapid and automatable approaches to organic analytical measurement including efforts in optical sensor design, flow injection immunoassay, capillary electrophoresis, supercritical fluid extraction technology and laboratory robotics. *The Gas Metrology Research Group* conducts research directed toward the preparation and measurement of primary gas standards. The Group is the Nation's primary reference laboratory for quantitative measurement methods and gas standards for a broad spectrum of areas including the atmosphere, vehicle emissions, and hazardous waste sites in which the gases range in concentration from the percent to the parts-per-trillion levels, and in complexity from the single to the multicomponent gas mixtures. The standards produced by the Group are recognized as being definitive by both industry and local, state and federal regulatory agencies. *The Mass Spectrometry Group* conducts research on the development of definitive measurement methods for clinically significant analytes in serum, on the use of mass spectrometry/mass spectrometry for quantitative analysis, on the application of mass spectrometry for structural determinations of biomolecules and on the development of methods for trace organic analyses of complex mixtures. *The Separation Science Group* directs research to provide a unified and coordinated approach for investigating physical and chemical processes that influence chromatographic separations and the use of these separation techniques, in a complementary manner, to separate, detect, and quantify individual organic species in complex natural matrices. A great deal of effort in this Group has continued to focus on investigations of the molecular interactions that occur during chromatographic processes and the design of "tailored" stationary phases for specific applications.

The Division's research program has four primary components: fundamental research and measurement activities in trace organic analytical chemistry and gas metrology (37%) supported from the Division's share of the NIST Congressional appropriation; research and measurement activities conducted in support of other Federal Agency programs on a reimbursable basis (40%); research and measurement activities in support of the NIST Standard Reference Materials Program (13%) which have resulted in the certification of 37 SRM/RMs in FY92 with another 11 in progress; and research and measurement activities undertaken on a cost reimbursable basis in support of U. S. Industry (10%).

Organic analytical chemistry continues to be a fertile research discipline that is critical to maintaining and improving public health, food/nutrition, the environment and U.S. industrial competitiveness. Scientists in the Division are making significant contributions to the development, theoretical understanding and application of new and emerging chemical measurement technologies such as analytical sensors, capillary electrophoresis, flow injection immunoassay and supercritical fluid and microwave-assisted solvent extraction and laboratory automation, while maintaining world-class capabilities in the chromatographic sciences, laser spectroscopy, organic mass spectrometry and gas metrology. The development and maintenance of these and other measurement technologies are vital to achieving and maintaining a world-leadership position in organic analytical measurement science.

Other Federal and State Government Agencies continue to comprise the Division's primary customer base, although interactions with, and support from, the industrial sector continue to increase. During the past year we were involved in 20 projects from 9 Federal and State Government Agencies. The two largest of these programs were related to providing analytical measurement quality assurance support for (1) epidemiological studies and cancer chemoprevention trials conducted by the National Cancer Institute (NCI) and (2) marine monitoring pollution programs being undertaken by the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA). The NCI program serves over 65 laboratories world-wide, involved in studies to determine the efficacy of selected fat-soluble vitamins and other phytochemicals as cancer chemopreventives. The NOAA/EPA program involves over 30 laboratories involved with the measurement of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and chlorinated pesticides in marine sediments and tissues.

In 1985, when the NCI program began, interlaboratory variability for the measurement of fat-soluble vitamins and carotenoid compounds in serum exceeded 50%. Even short-term intralaboratory variability of repeated measurements exceeded 10%, calling into serious question any purported correlations between preventive agent serum concentration and cancer prevention. NIST research and QA activities have fostered a five-fold improvement in interlaboratory measurement precision over the past seven years making it much more feasible to pool and compare data among epidemiological investigations and monitor the course of cancer chemoprevention trials. Interlaboratory imprecision is now less than 10% and both long and short term intralaboratory imprecision is less than 5% for participating laboratories. During the past year, in addition to serving as analytical measurement consultants to program participants and conducting and evaluating data from three interlaboratory studies, Division staff have: developed a novel liquid chromatographic stationary phase tailored for separation of carotenoid compounds; designed a flow-injection immunoassay system for the determination of estrogen hormones (breast cancer markers) in body fluids; provided analyses on 500 high priority serum samples from a twenty-year study; and developed and evaluated a robotically automated procedure for serum extraction.

As in the past, a significant portion of our interactions with industry has come via our collaborative activities with two industrial consortia and two professional organizations. The Consortium on Automated Analytical Laboratory Systems (CAALS) is headquartered at NIST and has nine U. S. based corporations and three Federal Agencies as members. Research efforts within the consortium are focused on the production of U. S. industry-wide automation compatible systems for chemical analysis. The Biotechnology Research and Development Corporation (BRDC) is a consortium of seven biotechnology companies with manufacturing facilities in the state of Illinois. Our collaboration with the BRDC involved the design, fabrication and evaluation of planar and fiber-optic waveguide phase-sensitive analytical sensors. The College of American Pathologists (CAP) is a professional organization of over 1000 physicians who specialize in pathology. The CAP oversees the performance of clinical laboratories in the U. S. through a variety of activities, including the administration of proficiency testing surveys. Two CAP-sponsored Research Associates work along with Division staff to develop definitive measurement methods for clinically-significant analytes in body fluids and to apply this technology in the value assignment of SRMs as well as proficiency testing pools and reference materials used in CAP programs. The Motor Vehicle Manufacturers Association (MVMA) is a trade association comprised of seven auto makers with manufacturing facilities in the U.S. The focus of our current program with the MVMA is concerned with the development and issuance of SRMs for measuring gaseous emissions needed to assist in automotive industry compliance with the 1990 "Clean Air Act". Our FY92 activities were directed toward the development of gas-phase standards for methanol and formaldehyde.

Our involvement with CAALS also led to research collaborations with two manufacturers of analytical instrumentation and a specialty gas company concerning supercritical fluid extraction technology, and with the CEM Corporation concerning microwave assisted sample preparation for food/nutrition and environmental analyses. CEM Research Associate Dr. Lois Jassie is working along with our staff to investigate: (1) saponification of food matrices for vitamin determination (e.g., infant formula) and (2) solvent extraction of marine sediment to remove organic contaminants. Initial experiments indicate that microwave assisted procedures can provide results comparable to traditional saponification procedures for determination of the vitamins in food and to Soxhlet extraction for the determination of contaminants in sediment. The microwave procedures offer the advantage of reduced time and quantity of solvent used for the solvent extractions. Future studies will focus on optimizing the conditions for these procedures (e.g., temperature, microwave energy, extractant, etc.).

In FY92 measurement activities within the Division contributed to the development or maintenance of approximately 50 SRMs including both simple and multicomponent cylinder gas mixtures, permeation devices for NO₂ and SO₂, clinically and nutritionally significant constituents in human serum and foods, drugs of abuse in both hair and urine, and both chromatographic calibration solutions and soil, sediment and tissue matrices for organic environmental pollutants. In addition, a new NIST standards program is being developed in partnership with EPA and Specialty Gas Companies to circumvent problems associated with both the availability and quality of the wide variety of gas standards that will be needed once the "Emissions Trading" provision

of the 1990 Clean Air Act takes effect. NIST Traceable Reference Materials (NTRMs) will be produced and distributed by Specialty Gas Companies with NIST oversight of the production and analysis. Certified concentration values will be assigned by NIST. Specialty Gas Companies will be allowed to develop and distribute NTRMs for any pollutant, concentration and balance gas combination for which an NIST SRM suite currently exists. NTRM concentration value assignment will be based on either comparison to or interpolation between existing SRMs. Uncertainties in NTRM concentration values will be slightly greater than those for corresponding SRMs, but should fall between 1.3 and 2.0%.

At the request of several recent evaluation panels, we have taken a close look at the number and scope of our collaborations, both internal and external. Many of our collaborations (15) involve academic or government research laboratories. They have been very intellectually stimulating and productive and we will attempt to maintain our level of involvement in this arena. During the past few years we have devoted extra efforts to increasing the number and quality of our collaborative research interactions with other Divisions within NIST and with U.S. industry. During FY92, five new collaborations have been established within NIST and twelve new collaborations were established or maintained with industry. Three of our industrial collaborations are being formalized through the establishment of CRADAs with the following companies: Paracelsian (a small biotechnology firm) to develop a flow-injection immunoassay system for estrogen hormones; Photonic Sensor Systems (a small optical products company) for development of strategies to immobilize antibodies on their proprietary planar waveguide interferometers; and the Union Carbide Corporation for development of a reference material for their proprietary use.

We plan to commence several new projects in FY93. A small portion of our efforts in chromatography and spectroscopy will be redirected toward the general area of real-time and/or in-field analytical measurement technology. We plan to begin a new program in rapid GC for chemical process measurements, and expand our current efforts in tunable diode laser spectroscopy of gaseous species, portable planar waveguide sensors, and flow-injection immunoassay. These new or expanded programs are in response to requests from the process analytical chemistry and environmental measurements communities. Other high-priority research areas for the coming year are: 1) stable protein immobilization technology; and 2) electrospray ionization of large molecules. The lack of adequate bonding chemistries for producing hydrolytically stable, covalent linkages of biologically active molecules to glass surfaces has been identified by representatives of 30 leading U. S. biotechnology companies as one of the top three problems limiting the development and marketability of commercial biosensors. Gaining a clearer understanding of the factors that affect the electrospray ionization process for large molecules will provide us with a new and powerful tool for characterizing biomolecules.

The overall strength of Division research and service efforts will be bolstered by the addition of three NRC Postdoctoral Research Associates: Dr. David Bunk, who will join the Mass Spectrometry Group and contribute to our development of electrospray mass spectrometry methods for determining biomolecule conformation; Dr. Janet Morrison, who will work with

staff in the Analytical Sensors and Automation Group and research the application of supercritical fluid extraction technology and capillary electrophoresis to forensic analyses; and Dr. Steven Page, who will work with staff in the Separations Science Group to investigate the properties of supercritical fluids pertinent to chromatographic separation.

Members of the Division received several honors this year. Dr. W.E. May was recognized by the Department of Commerce with the Gold Medal Award for his contributions to a major international effort to understand the roles of specific chemical species in the prevention of cancer. Dr. May also received the 1992 Percy L. Julian Award of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers in recognition of his contributions to trace organic analytical chemistry. Ms. R. Parris and Dr. M.M. Schantz received the Department of Commerce Bronze medal for the measurement of trace-level organic contaminants. Dr. L.T. Sniegowski received the NIST Measurement Services Award for her contributions to the development of definitive methods for the determination of cholesterol and glucose in human serum.

As stated previously, the work of the Division includes a broad range of research and service activities within the general areas of organic analytical chemistry and gas metrology. Programmatic activities include efforts directed toward health and clinical chemistry, food and nutrition, and the environment. Support of and collaboration with U. S. industry is on the increase. The Technical Highlights that follow provide details that reflect the high quality and broad impact of the Division's research programs.

**B. Selected Technical Activities
(Organic Analytical Research Division)**

1. Conceptualization and Implementation of Standardized Protocols for Automated Analytical Systems

F.R. Guenther and M. Salit (834)

As the drive to improve the quality of products, workplaces, and the environment grows stronger, the need to perform an increasing number of chemical analyses faster, cheaper, is predicted rise dramatically. These concerns are predicted to dramatically increase the number of samples in need of analytical work. Laboratory automation is increasingly being described as the only solution on the horizon for addressing the increasing sample workloads. However, the stand-alone design concept and the incompatibility of the incorporated computer hardware and software of modern instruments are chief obstacles to automating analytical laboratories. This lack of modularity makes the creation of fully automated analysis system a complex and expensive proposition. The Consortium on Automated Analytical Laboratory Systems (CAALS) was formed as a joint undertaking between private-sector firms, government agencies and NIST to address these issues.

In the CAALS automation world, the laboratory is made up of a hierarchy of controller and server modules that guide the analytical work being done on samples. The modules perform the tests and data analyses needed to deliver completed results to the requester. This hierarchy starts at the Laboratory Information Management System and is directed down through a Method Management Module (which translates tests to be performed into actual methods to be run on instruments), to the Test Station Controller (TSC) and its Standard Laboratory Modules (SLM). During the past year, four workshops have been held to specify behaviors of the TSC and the SLM modules. These two entities are the lowest level client/server pair of our hierarchical laboratory control system. The SLM represents the laboratory instruments that are "owned" and controlled by a TSC. The goal of CAALS is to make the SLM modular, such that an SLM from one manufacturer can be replaced with one from another manufacturer by simply switching the communications plug from one to the other (plug-and-play concept). To achieve this, a standard control protocol must be in place. This protocol must include standard communications, commands, and behaviors. NIST is implementing these concepts by building SLMs and TSCs to test the validity of the standards before they are presented to the analytical chemistry community.

The implementation effort has concentrated on software module development during the past year. Two reusable software libraries have been developed, which incorporate from 50 to 90% of the software that needs to be written to convert an existing instrument to an SLM. These software modules have been written in C++ for the Microsoft Windows operating environment, and consist of two libraries. The communications application program interface library, defines a common communication interface that can be used across processor platforms. This interface

was developed in collaboration with Sandia National Laboratories, and is to be implemented on PC and UNIX platforms. This will allow Sandia to port their UNIX software onto a PC DOS platform with a minimum of a reprogramming effort. In the future, this interface will be proposed as a standard to CAALS.

The other library developed here at NIST is an object library that encapsulates all standard SLM behavior into reusable C++ objects. This library intercepts the control dialogue from the TSC and in turn presents the CAALS interface to the TSC through return dialogue. All that is needed to convert existing laboratory instruments into an SLM is to create a "Glue" object. This Glue object sits on top of the SLM library and converts control commands into native instrument control tasks. The Glue object then transmits these tasks to the instrument over a dedicated communications line. Any response and/or status information coming from the instrument is communicated to the SLM library objects to handle in the CAALS specified manner, and transmitted to the TSC. This library isolates all CAALS SLM behavior into reusable software modules, thus minimizing the "Glue" code that must be written. Currently this code is being used in two implementation projects, the inorganic, and the organic projects, which will demonstrate several SLMs working together under the control of a single TSC. These projects are scheduled to be completed this coming year.

During the coming year we will continue to develop the SLM software modules as the CAALS workshops further define the specifications. We will also be starting a large effort to build a generic TSC that will start to control the SLMs using a script language to describe analytical chemistry tasks.

2. Fiber Optic Mach Zehnder Interferometer for Immunoassay

S.J. Choquette and L.L. Brown

Phase-sensitive interferometric, fiber-optic biosensors offer an attractive alternative to the more commonly implemented waveguide fluorescence techniques. There are several advantages to using a thermal assay with enzyme labels in this detection scheme: (1) greater immunity to fouling by sample components (such as proteins) since access to the evanescent wave is not required (2) inexpensive telecommunications fibers may be used and (3) common mode interferences, such as nonspecific protein adsorption are largely rejected by the dual-beam design. For these reasons, over the past year, we have investigated the development of bio-sensors based on the use of an all fiber-optic implementation of a Mach Zehnder interferometer in a thermal immunoassay.

The interferometer design incorporates a 0.5 mW frequency-stabilized HeNe laser, coupled into a 4-port fiber 3 dB beamsplitter, using standard positioners. The sense and reference fibers are mechanically spliced onto the output ports of the beamsplitter, which are shortened to reduce sensitivity to environmental noise. After passing through a 6 μ L flow cell, the sense and

reference fibers are mounted next to each other, and the output beams of each are allowed to overlap and interfere. The interference pattern is imaged onto a photodiode detector array and can be controlled by the fiber spacing and distance. The phase of this pattern is calculated using a discrete Fourier Transform with precalculated trigonometric terms for the particular spatial frequency imaged. This permits real-time sampling and phase calculation of the interference signal. With the current software and hardware developed, data rates of 30 Hz are obtainable.

Both enzyme and enzyme-labelled antibody assays are under development for use with the device. To demonstrate antibody-antigen binding, a sandwich assay was performed. Horse IgG was covalently immobilized to the surface of a stripped and silanized fiber using techniques previously developed at NIST. The sense fiber was then incubated with Anti-Horse IgG, covalently labelled with catalase enzyme. After 15 minutes, the unbound fraction was rinsed from the flow cell and a 20 mM peroxide solution was introduced into the flow cell. Within 2 minutes a 1 radian phase change was observed demonstrating thermal detection of the antibody-antigen complex. The baseline noise was approximately 5 milliradians, yielding a S/N of better than 200:1. Precision of replicate measurements however is poor, due to oxygen bubbles clinging to the surface, problems concerning antibody activity regeneration, and low immobilized antibody concentrations.

Future work will concentrate on refining the flow cell design, and on developing multifiber interferometers for multianalyte detection.

3. Design and Fabrication of Flow Injection Immunoassay Systems for Estrogen Hormones and Pesticides

L.L. Brown and S.J. Choquette

It is estimated that one in eight women will suffer breast cancer. Recent studies have shown that the manner in which an individual metabolizes estrogen may in fact be highly predictive of future breast cancer incidence. Measurement of two specific estrogen metabolites could aid in this risk assessment. One difficulty in measuring estrogen hormone metabolites in a routine test is that they are present at extremely low levels in body fluids, making current assays expensive and potentially inaccurate.

We are developing a new test for the estrogen metabolite 17- β -estradiol based on the successful theophylline Flow Injection Immunoassay (FIIA) technique designed at NIST and tested at the National Institutes of Health. Some changes are being made from our previous FIIA system to provide shorter per-sample analysis time and greater sensitivity. The new system employs a reactor column with covalently immobilized antigens (the hormone to be measured) which can be regenerated more rapidly by using acidic chaotropic reagents to break the antigen-antibody bond. The anti-estrogen antibody is noncovalently linked to the head group of a phospholipid molecule which is incorporated into a liposome membrane. From our FIIA modeling work, we

learned that the sensitivity of the assay is directly linked to the affinity of the antibody, and so the new assay scheme employs a high affinity monoclonal antibody to lower the detection limits to the physiologically significant levels. A Cooperative Research and Development Agreement has been established between NIST and Paracelsian, a small biotechnology company, to investigate this new assay format and to aid in the transfer of this technology. A patent application has been filed on the FIIA principle by NIST, and it is Paracelsian's future intention to license this patent and commercialize the estrogen measurement system.

To confirm the accuracy of the FIIA method for serum estradiol, the primary estrogen hormone, we are developing a GC/MS method. This method is not intended for large-scale routine measurements, but rather as a reference method for direct comparison with the FIIA method on a limited number of samples. The method involves addition of a deuterated form of 17β -estradiol to the serum, two solid-phase extraction steps, and analysis by capillary GC/MS. Experiments to date indicate that a standard quadrupole mass spectrometer may not be sufficiently sensitive for the low levels found, particularly in children. A new ion trap mass spectrometer has been acquired that should provide the required sensitivity.

We are also designing a FIIA system for chemical warfare agents as part of a collaborative effort with Chemical Research Development and Engineering Center, U.S. Army. A thiophosphate pesticide (parathion) is being used as a surrogate model compound because of both its structural similarity to the chemical warfare agents and the commercial availability of antibodies. In this system, a polyclonal antibody is immobilized onto silica particles and packed in a reactor column. The polyclonal antibody should exhibit reactivity for any compounds that are structurally similar to chemical warfare agents. In the new assay, pesticide is linked to the surface of the liposome membrane, and a competitive immunoassay is performed between the analyte and the labelled liposome for the antibody immobilized on the column. The system will initially be tested using purified aqueous samples of parathion and will later be adapted for measurement of groundwater and agricultural samples.

4. An Approach to the Development of a New Lipoprotein-Specific Serum Cholesterol Assay

M. Gray and A. Plant (831)

Coronary heart disease (CHD) is the number one cause of death in the U.S. Many studies have demonstrated the association of increased risk of developing CHD with increased levels of serum cholesterol. Recently it has been found that the proportion of cholesterol associated with different lipoprotein classes varies among individuals. Studies show that the amount of cholesterol associated with low density lipoproteins (LDL) compared to high density lipoproteins (HDL) is a better indicator of CHD risk than is total serum cholesterol. The latest research has shown the presence of a specific lipoprotein, lipoprotein(a) (Lp(a)), to be strongly related to CHD. Lp(a) is structurally similar to LDL in that they both contain the protein apo B-100, and

they are not separated from one another by conventional means. LDL levels are influenced by dietary intervention, Lp(a) levels are not. In addition, the amount of serum Lp(a) appears to be genetically determined; being higher in African American males than other groups in the United States.

Lp(a) is thought to account for the occurrence of CHD in many persons who appear to be otherwise normal. Since there is evidence to support the relationship between total serum cholesterol, Lp(a) protein and CHD, it is reasonable to assume that the amount of cholesterol associated with Lp(a) might provide a very powerful marker for genetic disposition to CHD. Measurement of serum Lp(a) protein is performed using immunoassay. There is currently no assay for determining the amount of cholesterol associated with Lp(a). Our goal is to develop such an assay.

Our approach involves the use of antibodies to immunospecifically select Lp(a) particles from other lipoproteins in serum, followed an enzymatic assay of the cholesterol associated with Lp(a). In order to validate the efficacy of our approach, we are currently developing assays for serum cholesterol associated with both Lp(a) and HDL. HDL-cholesterol assigned values (based on ultracentrifugation followed by the NIST ID/GC-MS method for cholesterol) will serve as benchmarks for evaluating the efficacy of our approach. The most popular clinical laboratory measurement approach to measuring HDL-cholesterol involves physical isolation of HDL from serum followed by a colorimetric enzymatic assay for bound cholesterol.

In addition to using antibodies for isolating the lipoprotein of interest, we are improving the enzymatic method for measuring cholesterol. Most enzymatic methods for cholesterol determination use colorimetric detection. We have optimizing a fluorescence detection approach to enhance sensitivity over that provided using colorimetric methods. Our investigation of the current cholesterol assay also includes comparing the effectiveness of two emulsifiers, Triton X-100 and Carbowax-8000, which are used to release lipoprotein-bound cholesterol and cholesteryl esters from the lipoprotein core. The two emulsifiers provide similar results when using colorimetric detection. However, in the fluorescence detection scheme Triton X-100 causes a significant optical interference. We have found the fluorescence detection approach using Carbowax-8000 to be the most effective, providing an order of magnitude greater sensitivity than the colorimetric assay. At our current sensitivity for cholesterol measurement, we should be able to use our approach to determine HDL-cholesterol at a typical concentration of 35 mg/dL. With additional studies to optimize the sensitivity of the fluorometric detection of cholesterol, we should be able to measure Lp(a) cholesterol at a typical concentration of 5 mg/dL in small volumes ($\leq 50\mu\text{L}$).

The next phase of the project involves designing an optimal approach for solid-phase immobilization of antibodies. We are currently investigating the appropriate types, sizes and surfaces of a solid phase to be used for immobilizing antibodies and trapping lipoproteins from serum.

5. Comparison of Carbon Dioxide, Fluoroform, and Chlorodifluoromethane Supercritical Fluid Extractants for the Recovery of PAHs from Environmental Samples

S.N. Chesler and A.P. Emery

Supercritical Fluid Extraction technology has been investigated as a means of automating the extraction of samples for subsequent trace organic analysis without the use of hazardous solvents. Supercritical CO₂ has been shown to provide recovery of nonpolar compounds such as fuel hydrocarbons from environmental samples. Increasing the scope of applicability of this "green technology" has been a priority of our group's activities in the past 2 years. We believe the largely unsuccessful application of SFE to more polar analytes has come from reliance by most researchers on relatively nonpolar carbon dioxide as the primary supercritical fluid extractant. We are investigating the extraction properties of fluids that possess permanent dipoles for the removal of more polar species from solid samples.

Recoveries that could be achieved for moderately polar analytes with CO₂, fluoroform (CHF₃), and chlorodifluoromethane (CHF₂Cl) were compared on a single test matrix, sodium montmorillonite clay, coated with $\mu\text{g/g}$ concentrations of three and four ring polycyclic aromatic hydrocarbons (PAHs). We found that in general, the SFE recovery decreased as the volatility of the PAHs decreased. A threshold in temperature and fluid density was identified for achieving recovery of the less volatile PAHs.

Of all of the extractants tested, CHF₂Cl was found to yield the highest PAH recoveries, providing results comparable to those obtained by the Soxhlet extraction. Perhaps the polarity of CHF₂Cl may be a better match to the moderately polar PAHs than the nonpolar CO₂ or the more polar CHF₃. The greater density of CHF₂Cl compared with the other fluids, may have also contributed to the higher PAH recoveries.

Results from these studies have been presented at 2 international symposia and a collaborative paper is in preparation with Professor Larry Taylor of Virginia Polytechnic Institute.

6. Evaluation of the Variance in Robotically Automated Serum Vitamin Extraction

S.N. Chesler, D. Duewer (837), and E. Schönberger (National Physical Laboratory, Israel)

As part of an NIST Quality Assurance Program for National Cancer Institute grantees involved in studies to determine the efficacy of selected fat-soluble vitamins as cancer chemopreventive agents, we have developed a robust, yet easily modified, protocol for the extraction of fat-soluble vitamins (retinol, α -tocopherol, and trans β -carotene) from human serum. We identified the sources and magnitude of variances encountered in using a Zymark II robot to provide serum

extractions and made hardware and software modifications required to minimize each of the detected variances. We have used one well-characterized lyophilized serum pool, Standard Reference Material 968a, for system optimization and variance determinations.

Numerous hardware and software modifications to the robotic system were required before adequate performance was achieved. Major modifications to the pipette delivery logic were necessary to assure precise and accurate transfer of sub-mL volumes of both relatively viscous serum and volatile ethanolic internal standard solution. Quantitative delivery was achieved by utilizing the prewet and airgap capabilities along with pause time variables offered by the Zymark software, with the addition of a "dummy" withdrawal and re-delivery of the serum and ethanolic reagent. Analysis of the optimized delivery protocol produced a precision for serum and ethanol delivery of 1.3% and 1.1% RSD, respectively in the analysis of 30 samples.

We also designed new hardware to improve the reliability and safety of the robotic extraction. The apparatus provided by the manufacturer for placing lids on sample tubes required significant time to remove/replace screw caps, and was accompanied by a relatively high incidence of capping failures. Hardware and software tools were developed which permitted both rimless and screw cap test tubes to be securely covered with unthreaded glass lids more rapidly and reliably. A custom waste disposal container was also designed to permit contained handling of biohazardous fluids and waste solvents.

Other determinants of variance in the system, including the number of replicates and the speed of the liquid-liquid vortex extraction and the effect of fluorescent room light have also been evaluated. Having successfully optimized the systems precision and accuracy for serum extraction, we are now planning to add an on-line analysis capability for evaluation of both sample throughput and long-term reliability.

7. Development of Tailored Stationary Phases for the Separation of Carotenoid Isomers

L.C. Sander and N.E. Craft

The chromatographic properties of commercial columns used in reversed-phase liquid chromatography often differ markedly, even among columns presumably of the same type. To a large extent, column selectivity is controlled by bonded phase morphology, particularly for solutes with similar size and shape. The selection of suitable substrate properties (particle size, pore size, and surface area) and surface modification procedures (ligand and phase type) permits wide variations to be created in the retention properties of the resulting bonded stationary phase. An understanding of the processes that govern retention permits prudent selection of these variables for the production of phases tailored for a specific application.

The separation of geometric isomers is frequently difficult since their physical and chemical properties are usually very similar. An example of such a class of compounds are the

carotenoids. Carotenoids are polyprenoids containing a series of conjugated double bonds and may contain oxy, epoxy, and/or furanoxo substituents. Changes in the position of the substituents and in the cis/trans orientation at the double bonds give rise to numerous isomers and related compounds. The relative abundance of these isomers differs among natural sources such as fruits and vegetables. Since carotenoids are of great current interest in studies concerning the reduction of the incidence of several diseases, including cancer, separation and measurement of the individual carotenoid compounds is of great importance.

The subtle differences in the structures of carotenoid isomers provide only a limited basis for separation. The difficulty in developing LC methods for the analysis of carotenoids is further aggravated by lot-to-lot variations in selectivity that occurs among stationary phases from a single manufacturer. Such variations may have no effect for the majority of applications for columns packed with the stationary phases, and therefore may go undetected in normal column quality control tests.

Among commercial C_{18} columns, polymeric phases often exhibit better selectivity toward nonpolar carotenoid hydrocarbons than monomeric C_{18} phases. Unfortunately, the absolute retention of polymeric phases is limited compared with monomeric phases, making the separation of early eluting polar carotenoids difficult. Conversely, monomeric C_{18} phases often strongly retain polar carotenoids, but are less able to separate nonpolar hydrocarbon carotenoids. The goal of this research was to design new bonded phases incorporating the favorable properties of both monomeric and polymeric C_{18} phases, to improve separations of carotenoid mixtures.

Several approaches were combined in the development of the tailored "carotenoid column." Polymeric phases with high absolute retention were prepared using a silica substrate with novel characteristics. Unlike most wide pore substrates, IMPAQ™ silica has a relatively large specific surface area ($\sim 250 \text{ m}^2/\text{g}$). Polymeric C_{18} phases prepared on this substrate exhibited greater absolute retention than is typical for comparable phases on low surface area substrates. Retention was further enhanced by using a longer carbon chain length silane reagent: trichlorotriacontylsilane (C_{30}) in place of trichlorooctadecylsilane (C_{18}). Research involving the separation of polycyclic aromatic hydrocarbon (PAH) isomers has indicated that column "shape selectivity" is improved with longer chain length phases. The C_{30} silane has the dual effect of increasing carbon loading (and thus retention) while enhancing shape selectivity toward carotenoid isomers. Because carotenoids consist of polar and nonpolar species, the potential for polar solute/stationary phase interactions exists. The effect of silanol interactions was studied and better separations of polar isomers were achieved for phases that were *not* deactivated. Thus, silanol activity contributes to the separation of polar carotenoids.

Columns were prepared with these combined features, and the retention behavior was studied for carotenoid mixtures. Significantly enhanced separations of polar and nonpolar carotenoid isomers were achieved. The development of these tailored stationary phases should prove valuable not only for analytical measurements of carotenoid isomers, but also for the purification of carotenoid compounds on a preparative scale.

This research should have immediate application for National Cancer Institute programs that require the determination of carotenoid compounds in human serum. It is anticipated that the use of tailored carotenoid columns will facilitate the development of robust analytical methodology, and result in the improvement of measurement precision and accuracy and interlaboratory comparability. Commercial interest in this stationary phase technology is also anticipated, and patent potential is under examination.

8. Update on Carotenoid and Vitamin Measurements in Human Serum and Food Samples

N.E. Craft, J.M. Brown Thomas, S.A. Margolis, and K.S. Sharpless

Last year we described our efforts in the measurement of vitamins and carotenoid compounds in serum and food matrices. Since that report, we have developed an improved liquid chromatographic (LC) method for carotenoid measurements, reissued Standard Reference Material (SRM) 968 "Fat-Soluble Vitamins in Human Serum", and expanded our vitamin SRM efforts to include food matrices. The improved LC method for carotenoid measurements permits the simultaneous measurement of retinol, retinyl palmitate, α -, δ -, and γ -tocopherols, lutein, zeaxanthin, α - and β -cryptoxanthin, lycopene, and α - and β -carotene with precision of repeat measurements over time of 2.5% to 5.5% RSD. This method is currently being used to measure vitamins and carotenoids in serum samples from several high priority National Cancer Institute cancer epidemiology studies.

SRM 968a "Fat-Soluble Vitamins in Human Serum" was certified during the past year and has certified values for vitamins (A and E) and β -carotene in human serum. The SRM consists of six vials of lyophilized serum; two each of low, medium, and high physiological concentrations. SRM 968a was certified using three different NIST LC methods along with results from seven laboratories that have participated in the NIST/NCI Fat-Soluble Vitamin Quality Assurance Program. Information values are also provided for lutein, zeaxanthin, β -cryptoxanthin, trans-lycopene, total lycopene, α -carotene, trans- β -carotene, γ -tocopherol, and cholesterol. This material is being used worldwide for providing analytical measurement quality assurance for clinical studies that require serum vitamin measurements.

We have initiated the certification of two new SRMs related to vitamins in food matrices: SRM 1846 "Infant Formula" and SRM 2382 "Carotenoids and Vitamins in Food". SRM 1846 was stimulated by the Infant Formula Act of 1980 which regulates the upper and lower limits of certain vitamins in infant formula and requires that infant formulas be labeled with nutritional information. SRM 1846 is being prepared to help manufacturers comply with Food and Drug Administration regulations. The material consists of a spray dried milk-base powder that has been supplemented with vitamins prior to agglutination and packaging. The fat-soluble vitamins will be certified using three approaches: traditional alkaline hydrolysis followed by reversed-phase LC, enzymatic hydrolysis followed by reversed-phase LC, and gel permeation

chromatography (GPC) coupled to normal-phase LC. The traditional hydrolysis will permit the measurement of the total free vitamin A, vitamin E, and vitamin D while losing vitamin K in the alkaline environment, whereas enzymatic hydrolysis will permit the measurement of the total free forms of all four vitamins. The coupled GPC/normal-phase LC approach will permit the measurement of the individual forms of the vitamins as they occur in the formula (i.e., retinol, retinyl acetate, retinyl palmitate). LC methods have also been evaluated to measure water-soluble vitamins, i.e., ascorbic acid (vitamin C), nicotinic acid, nicotinamide, pyridoxine, thiamine, and riboflavin, in the infant formula matrix.

More recently, the Nutritional Labeling and Education Act of 1990 has been passed and requires food manufacturers to provide information on the product label about the content of specific nutrients. This legislation has created a new demand for reference materials in food matrices with certified concentrations of nutrients. SRM 2382 "Carotenoids and Vitamins in Food", is being prepared to meet the needs. This SRM is a mixture of pureed vegetables, fruits, and infant formula that will have certified concentration values for selected carotenoids and vitamins. Individual baby foods were assayed for carotenoid content and a "recipe" was developed that provided an acceptable profile of a number of carotenoids. Powdered infant formula was incorporated to elevate the endogenous levels of vitamins. An infant formula company has prepared a pilot batch of this material to assess feasibility and analyte stability. It is envisioned that more food-related reference materials will follow and that a quality assurance program for measurements associated with nutritional labeling requirements will be established.

9. Synthesis of Tocol, a Useful Internal Standard for Determinations of Fat-Soluble Vitamins

A. Cohen and N.E. Craft

Many of the fat-soluble vitamins and related compounds may act as cancer-preventive agents. The National Cancer Institute supports research that investigates the relationship between serum levels of these compounds with the incidence of cancer. NIST has established an on-going program for providing measurement quality assurance to laboratories involved in cancer chemopreventive and/or epidemiology studies.

Tocol has been found to function as an excellent internal standard for the quantitative measurement of retinoid- and tocopherol-related compounds, using high performance liquid chromatography. We found that the extraction efficiency and the stability of tocol are similar to that of retinol and tocopherol. Tocol is structurally similar to the tocopherols, lacking only the alkyl groups attached to the aromatic ring. It is an oily liquid at room temperature and is subject to oxidation if preventive steps are not taken, thus making it difficult to prepare in a purified state. Because tocol is beneficial for measurement of these vitamins and is not commercially available, a program has been initiated to provide high purity tocol as a reference material.

After an extensive literature search, a promising synthetic approach was identified. Tocol was synthesized by boiling hydroquinone and phytol in a mixture of benzene and formic acid under a nitrogen atmosphere. After work-up, the crude syrup was vacuum distilled. Thin-layer chromatography (TLC) of the distillate and visualization with a phosphomolybdic reagent, indicated over a dozen impurities. In order to avoid extensive chromatography, a portion of the syrup was derivatized with 4-phenylazobenzoyl chloride, following a published procedure, which should have produced a solid that could be recrystallized to remove impurities. The recrystallized product would then undergo hydrolysis and distillation to yield pure tocol. Unfortunately the solid was not obtained, only the crude 4-phenylazobenzoate oil. Based upon a method described in the literature, an alternate approach was tried. Another portion of the crude tocol syrup was derivatized by acetylation, distilled, and hydrolyzed to tocol which was also distilled. There was substantial improvement in the purity of the tocol, as determined by TLC, but additional chromatographic procedures may be necessary to remove the remaining impurities. Once the material has been satisfactorily purified and evaluated, it then can be made available to the fat-soluble vitamin measurement community.

10. Stability of Cholesterol in Food Matrices

A. Cohen, P.M. Ellerbe (College of American Pathologists), L.T. Sniegowski, and M.J. Welch

Blood cholesterol levels have been linked to the incidence of heart disease, the number one cause of death in the U.S. For many individuals, blood cholesterol levels are affected by the cholesterol and fat content of their diets. For that reason, the Nutrition Labeling and Education Act of 1990 requires the food processing industry to include cholesterol content in the nutrition information given on the label. NIST has three Standard Reference Materials (SRMs) that are used by the food industry to validate the accuracy of methods used for determining the cholesterol content in food. These SRMs are: SRM 1548, Total Diet; SRM 1845, Whole Egg Powder; and SRM 1563, Coconut Oil. Cholesterol content in these SRMs were established using a modification of the isotope dilution, gas chromatography/mass spectrometry (ID/GC/MS) definitive method for serum cholesterol.

Recently, the Standard Reference Material Program (SRMP) received several questions about the current level of cholesterol in SRM 1548, which had been originally certified in 1988. Remeasurement by the ID/GC/MS method found that the cholesterol concentration had dropped considerably since 1988 and was no longer homogeneously distributed throughout the SRM lot. In 1988, we found the cholesterol level to be 795 $\mu\text{g/g}$ of freeze-dried food composite; in 1992, five vials analyzed had concentrations ranging from 190 to 360 $\mu\text{g/g}$. At the same time, the egg powder, SRM 1845, was also remeasured and its concentration was essentially unchanged since the original certification measurements in 1988. SRM 909a, Human Serum, was run as a control in these experiments. The cholesterol results were in agreement with the certified values.

Further investigation found that the level of irradiation used to sterilize the total diet material was much higher than that used for the egg powder and that cholesterol is known to oxidize when irradiated under certain conditions. Subsequently, full scan GC/MS runs found evidence of cholesterol oxidation products in the total diet material. Because of these findings, SRM 1548 is no longer certified for cholesterol concentration. During FY93, the stability of cholesterol in the third food matrix SRM, coconut oil, will be measured, although no significant changes are expected because the nature of the matrix and the processes used to prepare the SRM are unlikely to contribute to cholesterol degradation.

11. Determination of Polycyclic Aromatic Hydrocarbons in Combustion Samples

B.A. Benner, Jr. and S.A. Wise

At the request of the U. S. Environmental Protection Agency (EPA), we are continuing to characterize different combustion sources for polycyclic aromatic hydrocarbons (PAHs). The characterization of different combustion sources for PAHs is an important endeavor in environmental chemistry, particularly when one considers the large number of different sources as well as the continuous improvement of analytical measurement technology for the separation and measurement of individual PAH isomers. In the FY91 annual report, results from the analyses of ten combustion-related samples were described. Those ten samples were representative of the following combustion sources: residential wood burning, automotive emissions, diesel exhaust, aluminum smelter emissions, roofing tar, coke oven emissions, and polyethylene incineration emissions. The samples were analyzed using gas chromatography with mass spectrometric detection (GC-MS) for the determination of selected PAHs. The results of the PAH measurements are being used in conjunction with EPA mutagenic activity data to determine which family or individual PAHs are responsible for the mutagenic properties of combustion-related emissions.

During the past year nine additional combustion-related samples were analyzed as part of this effort including two wood burning extracts, five diesel source samples, a coal tar pitch, and a carbon black extract. For the GC separation of the PAHs, we used a liquid crystalline stationary phase to allow the measurement of several PAH isomers that are not resolved on the nonpolar stationary phase columns typically used for PAH determinations.

During this study eight different diesel soot samples have been characterized including emissions from both heavy-duty and light-duty engines. The relative ratios of several of the PAH isomers varied significantly in this series of diesel samples. For example, the ratio of fluoranthene-to-pyrene (four-ring isomers of molecular weight 202) varied from 1 to 5 for the five light-duty diesel engines and varied from 10 to 64 for the three heavy-duty diesel engines. For this same series of eight diesel samples, the ratio of chrysene-to-benz[a]anthracene and chrysene-to-triphenylene (four-ring isomers of molecular weight 228) varied from 1 to 26 and 1 to 3, respectively; and the ratio of benzo[b]fluoranthene-to-benzo[k]fluoranthene (five-ring isomers of

molecular weight 252) varied from 2.5 to 22. These variations in isomer ratios for the different diesel samples may be useful in differentiating diesel emissions (e.g., light-duty vs. heavy-duty engines or old engine design vs. current engine design).

Of the eight diesel samples analyzed, one sample was significantly different in the relative ratios of the PAH isomers. This diesel soot sample was collected from a diesel-powered forklift with a newly designed filter system to remove the emission particulate matter. For this sample the concentrations of several PAHs were enriched (e.g., fluoranthene, chrysene, benzo[b]fluoranthene, and indeno[1,2,3-cd]pyrene) relative to the other PAH isomers, when compared with the other diesel samples characterized. EPA has found this particular diesel sample to have very high mutagenic activity. Based on the high mutagenic activity and the indication that this material may be more representative of future diesel emissions, EPA has requested that NIST use this diesel soot sample to prepare a diesel extract as an SRM. We have obtained 10-15 kg of this material for that purpose. SRM 1975, Diesel Particulate Extract, will be characterized with respect to both its PAH content and mutagenic activity, thereby providing an SRM for both bioassay and PAH measurements.

12. Development of Non-Methane Organic Compound SRM for Ozone Precursor Studies

W.R. Miller and G.C. Rhoderick

Non-Methane Organic Compounds (NMOC's), due to their reaction with certain atmospheric gases such as nitric oxide from automotive exhaust, have been shown to have a major role in the generation of photochemical smog. This has led to an increase in both the number and scope of federal and state programs implemented to monitor these pollutants. A cylinder gas Standard Reference Material (SRM) containing the key NMOC's has been requested by both EPA and the Motor Vehicle Manufacturers Association to support measurements within these programs.

During the past three years, the Gas Metrology Research Group has been preparing and certifying NMOC gas mixtures for both the U.S. EPA and the California Air Resources Board (CARB). Primary standards have been prepared and stored at NIST during this period. Periodic re-analysis of these standards and the EPA and CARB mixtures have shown that the NMOC's exhibit excellent stability for over three years. Based on these studies, we think it feasible to prepare and certify a NMOC SRM mixture to meet the needs of the EPA and state of California programs.

The SRM will contain 15 NMOC's at a nominal concentration of 10 nanomol/mol (ppb) with a targeted uncertainty of ± 1.0 ppb. Ultra high purity nitrogen will be the matrix gas. The compounds to be included in this mixture are the following normal and branched alkanes, alkenes and aromatic hydrocarbons: ethane, propane, propene, n-butane, iso-butane, 1-butene, iso-butene, n-pentane, iso-pentane, 1-pentene, n-hexane, n-octane, n-decane, benzene, toluene and ortho-xylene.

The NMOC SRM mixtures will be prepared by NIST personnel in 4.25 m³ (150 cubic foot) aluminum compressed gas cylinders which have been commercially treated to passivate the interior surfaces. A high concentration standard containing a nominal 1 μ mol/mol (ppm) of each component will be prepared and analyzed against existing primary standards. Once the concentration of each component is known, an aliquot of this mixture will be transferred into each of the candidate SRM cylinders and diluted to the 10 ppb level with ultra-high purity nitrogen.

One of the candidate SRM cylinders will be analyzed against new and existing primary standards. This batch standard will then be intercompared with the other candidate SRM cylinders to determine the batch homogeneity. This process will be repeated after a three month period to assess compound stability. If no instability is observed, the SRM will be assigned a value and certified.

13. Standards for Pollution Trading

W.D. Dorko, F.R. Guenther, W.E. May, and W.J. Thorn

The 1990 Amendments to the Clean Air Act require manufacturing industries to substantially reduce their air toxic emissions by 1995. Rather than promulgating regulations, EPA has given companies the freedom to choose their own control technologies for meeting mandated emissions reductions with the bottom-line reward being the ability to sell any extra "compliance allowances" to other companies. This financial incentive based concept is being hailed by all parties--EPA, utility companies, and environmental groups--as an innovative and viable means for encouraging industries to reduce their air toxic emissions in an expeditious manner.

With air pollution allowances and a financial incentives for not exceeding them, there will be a need for very stringent and accurate monitoring of emissions. Each regulated facility will be required to install continuous emission monitors (CEMs) which will have to be calibrated on a frequent basis with calibration gas mixture standards. The EPA has determined that CEMs should be calibrated with an uncertainty not exceeding 2% in order to adequately measure compliance and facilitate equitable trading of emissions. In order to achieve this level of measurement uncertainty, calibration gas standards of high and uniform quality must be readily available.

Currently, CEMs are calibrated using EPA "Protocol Gases" produced upon demand by Specialty Gas Companies according to an EPA "Protocol Gas" document. This procedure has resulted in standards of variable quality among "Protocol Gas" manufacturers. EPA has conducted annual audits which have shown the variability among Protocol Gases to typically be 1-3%, but as high as 20% on occasion. Standards of this quality are clearly not sufficient for monitoring compliance with "Clean Air Act" targets.

The NIST role in this arena is two-fold; 1) to provide high quality measurements standards to serve as benchmarks for the mandated measurement and monitoring activities and 2) to provide measurement standards to facilitate equitable trade. NIST facilities are limited relative to those needed to produce and certify the large volumes of gaseous pollution standards needed to calibrate CEMs in industrial facilities.

During the past year, NIST has worked closely with EPA to revise and improve the Protocol Gas Standards program. These interactions have resulted in a new NIST standards program, in partnership with the Specialty Gas Industry, to address problems concerning both the quality and the quantity of gas standards needed to support monitoring and measurement activities associated with the "Clean Air Act". NIST Traceable Reference Materials (NTRMs) will be produced and distributed by Specialty Gas Companies with NIST oversight of the production and involvement with the analysis phases. Certified concentration values will be assigned by NIST. Specialty Gas Companies will be allowed to develop and distribute NTRMs for any pollutant, concentration and balance gas combination for which an NIST SRM suite currently exists.

The new program will require that commercial suppliers of gas standards produce candidate NTRM cylinders in batches, provide NIST with data concerning batch homogeneity, and submit to NIST randomly selected cylinders from the batch for measurement. Based on both company and NIST measurement data, NIST will issue NTRM certificates (cosigned by EPA) for all cylinders in the batch. Concentration value assignment will be based either on comparison to, or interpolation between existing SRMs. Uncertainties in NTRM concentration values will be slightly greater than those for corresponding SRMs, but should fall between 1.3 and 2.0%.

The NTRM program should provide both Specialty Gas suppliers and end users with a continuous supply of high quality toxic gas calibration standards with well-defined traceability to NIST.

14. Stability Studies of Nitrogen Dioxide Gas Mixtures and Certification of a New NO₂ SRM 2660

W.D. Dorko, R.L. Sams, and W.J. Thorn III

Nitrogen dioxide (NO₂) is formed spontaneously in air from nitric oxide (NO) which is exhausted from mobile pollution sources (e.g., automobiles) and from stationary sources (e.g., power plants) as a byproduct of their combustion processes. Concentrations of NO₂ are monitored because of its acidity when mixed with water vapor (acid rain) and its contribution to the production of smog and high ozone levels in urban environments.

In the early 1980's, NIST developed cylinder gas mixture Standard Reference Materials (SRMs) 2653, 2654, 2655 and 2656 containing NO₂ in air at nominal concentrations of 250, 500, 1000 and 2500 $\mu\text{mol/mol}$ (ppm). These mixtures were developed for use in the calibration of equipment for EPA required monitoring stationary sources. Later in the 80's, work commenced

to determine the possibility of providing NO₂ SRMs at lower concentrations. Cylinder gas mixtures at the 100 ppm level, as well as some of the originally certified higher concentration SRM mixtures, were observed over time to ascertain concentration stability. The instrumentation used both at NIST and in the monitoring community detects total NO_x (NO, NO₂ and HNO₃) and not just NO₂. What had been established during the original certification process was that the NO₂ content of the SRMs was really a combination of NO₂ and HNO₃ (nitric acid), where the nitric acid originated from the reaction of NO₂ and water inside the cylinders. Since the analytical instrument determined total NO_x, a difference method had to be used to establish the amount of nitric acid. A nylon filter scrubs the acid from the gas stream. By observing the instrument response when the sample stream is unscrubbed, and then scrubbed, one can determine the amount of nitric acid. The applicability of the scrubber was verified on several occasions by a spectroscopic method, tunable diode laser absorption spectroscopy, which responds to nitric acid directly. Stability studies have shown that the NO_x content is more consistent and stable with time than NO₂. For example, in one 100 µg/g (ppm) test mixture, the 1988 values were 101 ppm NO_x and 2 ppm nitric acid while the 1992 numbers are 101 ppm NO_x and 4 ppm nitric acid. Observing samples of the mixtures at the 250, 500 and 1000 ppm levels over a three to eight year period produced similar results. The best NO₂ SRM would be one with no nitric acid, but since this cannot be achieved, mixtures with low amounts of the acid are acceptable. However, proper use of the SRM requires a knowledge of the proportion of each.

With the above information at hand, a batch of candidate SRM mixtures were prepared at a nominal concentration of 100 ppm NO₂ in air. These mixtures were prepared in cylinders specified to be very dry, in order to avoid acid formation. The NO₂/NO_x concentration values were verified using a series of gravimetrically calibrated NO₂ permeation tubes and the NIST primary suite of NO reference cylinders.

Measurements have been completed on all twenty-five (25) cylinders of SRM 2660. Based on results using the two methods described above, all cylinders have concentrations of NO_x close to 100 ppm. Further evaluation of each cylinder has shown that after 18 months, these mixtures contain on average 96 ppm NO₂ and 4 ppm nitric acid. Consistent with the stability findings discussed above, experimental data on these mixtures show that the total NO_x concentration is stable over the 18 month "hold period." These cylinder mixtures have been determined to be suitable for SRM use since the NO_x value is stable and the nitric acid level is sufficiently low.

15. Development of Methanol Gas Standards for Auto Emission Measurements

G.C. Rhoderick

Recent amendments to the Clean Air Act have mandated that vehicles in the United States with internal combustion engines burn "clean fuel". One such fuel which is receiving a lot of attention is a mixture of methanol and gasoline. In order to determine the combustion efficiency

of an auto using such a fuel, the amount of methanol being exhausted must be determined. Methanol in air standards are needed to calibrate the instruments used to measure the exhaust.

This past year, NIST has been involved in a research program to determine the feasibility of preparing stable gas mixtures containing methanol, and to study the optimum method for analytically sampling methanol from a gas stream. A gas mixture containing methanol at 100 $\mu\text{mol/mol}$ (ppm) and propane at approximately 45 ppm in nitrogen was prepared. Since it is well known that propane in gas mixtures is stable, this compound was used as an internal check to measure the stability of the methanol over time. The propane was also used to show that the analytical system remained under control and operating properly.

The sample was injected onto the gas chromatographic column using a stainless steel gas sampling valve equipped with a 0.5 mL stainless steel sample loop. Several different types of regulators and sample lines were tried to determine which combination gave the most stable and precise results. After many experiments, it was determined that a stainless steel low dead volume regulator equipped with a stainless steel needle valve was the best device to use on the cylinder. The data show that the sample line material does not appear to be critical, with stainless steel, copper, nylon and teflon all being tested. Also, the length of the sample line does not appear to be significant with lengths up to 15 feet being tested. Several different sample flow rates were tested and the lowest rate that produced stable and precise results (80 mL/min) was used. The analytical results show that when sampling the very first cylinder of the day it can take 45 - 90 minutes injecting a sample every 5 minutes to obtain a consistent peak integration. For subsequent cylinders, four or five injections are needed before the beginning of a stable response is achieved. Using these procedures analytical imprecisions of 0.5 % or less are achievable.

Several gas standards containing methanol have been prepared, in both air and nitrogen matrices, at concentrations ranging from 5 to 100 $\mu\text{mol/mol}$. These standards have been intercompared with one another over the past 8 months and the data have been reduced using regression analysis. The concentration of methanol in each mixture has then been estimated from the regression lines. The results, for the air standards only, show that the average residual between the theoretical and estimated concentration is 1.5%. The imprecision at the low concentration level, 5 $\mu\text{mol/mol}$, is 1% where as it was 0.4% or better at the higher concentrations. This appears to effect the low end in the regression and the residual is much greater, effecting the overall residual. If the 5 $\mu\text{mol/mol}$ standard is deleted from the line fit of the air and nitrogen standards together, then the average residual is 0.6%.

This research has shown that it is feasible to prepare accurate and stable mixtures of methanol in either an air or nitrogen matrix. With care, aliquots of methanol mixtures can be quantitatively removed from gas cylinders. This research provides the foundation for certifying methanol mixtures for use in calibrating instruments for monitoring methanol fueled automobile emissions.

16. Penetration Studies of Drugs of Abuse in Hair

L.T. Sniegowski, M.J. Welch, E. White V, G.J. Gillan (837), and C.J. Zeissler (837)

There is considerable interest in the analysis of hair samples for drugs of abuse, because the window of detection is much larger than that from the analysis of body fluids and sampling procedures are non-invasive. However, there are important questions, such as how well laboratories can measure drug levels in hair, that must be answered before hair analysis is widely accepted as an alternative to urine drug testing. The precision and accuracy of methods used by laboratories for hair analysis can be evaluated by the use of reference materials prepared by soaking blank hair samples in solutions containing the compounds of interest. It is of interest to determine if differences in hair type, e.g. racial, color, chemical treatments, will result in variations in drug penetration and incorporation in hair reference materials.

In this study, secondary ion mass spectrometry (SIMS) was used for imaging the cross-sectional penetration of drugs in soaked hair. The compound selected for this work was 3-fluorococaine. It is structurally very similar to cocaine and is expected to behave much like cocaine in penetration studies, but the addition of the fluorine atom makes this compound readily detected by SIMS. It was prepared from the reaction of 10 mg of ecgonine methyl ester hydrochloride hydrate with 3-fluorobenzoyl chloride, and purified by the use of solid phase extraction cartridges. The synthetic yield of 3-fluorococaine was approximately 70%.

Hair samples were prepared by soaking blank hair in a solution of 5 mg of 3-fluorococaine in one mL of dimethylsulfoxide for periods of seven to nine days. Different types of hair were soaked. Two of the hair samples, oriental hair and chemically-treated caucasian hair, have now been examined by SIMS.

Hair samples, sliced and mounted to permit cross-sectional analysis in a secondary ion microscope/microprobe, were subjected to Cs^+ bombardment while monitoring negative secondary ions. Resolution with this technique is approximately $1\ \mu\text{m}$. The F^- secondary ion signal was used as a marker to localize the position of the molecule. In both the hair samples examined, the 3-fluorococaine was localized mainly in the periphery of the hair, penetrating 10-20 μm below the surface out of a total cross-section of 75-100 μm .

We are seeking to initiate a collaboration that would provide us with human hair that has 3-fluorococaine incorporated through ingestion. This will allow us to compare the results from ingestion studies with the results from soaking this compound into hair. Experiments, such as those at the University of Utah in which mice serve as hosts for living human hair follicles, may provide us with a means to acquire such hair.

17. Recent Activities Regarding the Development of Drugs of Abuse SRMs for Urine and Hair

L.T. Sniegowski, M.J. Welch, P.M. Ellerbe (College of American Pathologists), and S. Tai (College of American Pathologists)

Drug testing programs are in widespread use in the criminal justice system, in the workplace, and in pre-employment screening. The outcome of such tests can have a profound effect on the individuals involved. Thus it is extremely important that such tests be accurately performed. Accuracy in drug testing requires not only determining whether drugs of abuse or their metabolites are present, but also accurately determining the concentrations of these substances. NIST, in cooperation with the College of American Pathologists (CAP), has developed a series of Standard Reference Materials (SRMs), with certified concentrations of some of the substances most commonly tested for in urine drug testing programs, to assist laboratories in assuring the accuracy of their methods.

For the first SRM in this series, SRM 1507 - Marijuana Metabolite in Urine, the certified concentration was found to decrease with time. Therefore, we carefully monitor the stability of these SRMs and provide updated certified values as needed. Three of the four NIST drugs of abuse in urine SRMs and a reference material (RM) for amphetamines in urine from the CAP, were tested for stability this past year using GC/MS. All three levels of each of the SRMs (1507b - marijuana metabolite, 2381 - morphine and codeine, and 2382 - morphine glucuronide) were found to be unchanged from measurements made one year earlier. Only for one of the amphetamine levels in the CAP RM were the new results outside the uncertainty limits around the certified value. Because there was no conclusive evidence for degradation in this material, the uncertainty limits were broadened for this one level.

A new multidrug-in-urine SRM is being developed. This SRM consists of a single level of each of the seven substances that are mandatory in the National Institute on Drug Abuse (NIDA) workplace drug testing program. For each substance, the level is within 10% of the NIDA cutoff, i.e., the concentration below which a specimen is judged to be negative. As this is the critical point for laboratory accuracy, many laboratories have expressed a strong interest in this SRM. During this past year, three batches of materials were evaluated. The first two were rejected because some of the analytes failed the within 10% criteria. The third batch appears to meet the criteria and has been accepted. The certification measurements are now beginning and will involve GC/MS and LC or LC/MS measurements at NIST, and measurements using the prescribed DOD methods by a group of military drug testing laboratories.

Hair has been shown to retain evidence of drug use for long periods of time. Consequently, many laboratories involved with drug testing are investigating the efficacy of hair analysis for determination of drug abuse. This past year NIST issued two RMs to assist laboratories in making accurate measurements in this area. Both materials consist of human hair with concentrations of cocaine, benzoylecgonine (cocaine metabolite), morphine, and codeine

determined using GC/MS at NIST. One material is a powder that is useful for laboratories testing the accuracy and precision of their measurement methods. The other is a short segment material that can be used to test their overall procedure, including washing, extraction, and analysis.

18. **A New SRM for Organic Contaminants in Marine Mammal Tissues: SRM 1945, Organics in Whale Blubber**

M.M. Schantz, B.J. Koster, and S.A. Wise

Because of increasing concerns about the effects of marine pollution on the health of marine mammals, the National Oceanic and Atmospheric Administration (NOAA) is developing a broad program consisting of four components: stranding networks, the National Marine Mammal Tissue Bank, monitoring, and quality assurance. As part of these monitoring and tissue banking efforts, a number of laboratories are involved in the analysis of marine mammal tissues to measure the levels of various trace elements and organic contaminants. In addition numerous other laboratories world-wide are involved in similar analyses of marine mammal tissues. To assess the accuracy and comparability of results among various laboratories for marine mammal tissue analyses, NOAA and the National Institute of Standards and Technology (NIST) have initiated a quality assurance (QA) program for analytical measurements of contaminants in marine mammal tissues. This QA program consists of: (1) preparation, analysis and distribution of marine mammal tissue control materials; (2) interlaboratory comparison exercises among NIST and other laboratories involved in NOAA projects related to marine mammal tissue analyses; and (3) development of Standard Reference Materials (SRMs) for use in the analysis of marine mammal tissues.

In response to the third component of the QA program, a new SRM for organic contaminants in marine mammal tissues has been prepared: SRM 1945, "Organics in Whale Blubber." In September 1991, approximately 15 kg of blubber was collected from an adult pilot whale which stranded on Cape Cod. The blubber tissue was frozen and shipped to NIST where it was stored at liquid nitrogen vapor phase temperatures. Later, the blubber was cryogenically pulverized and homogenized in Teflon mills to provide a frozen powder-like material similar to marine mammal tissue samples routinely analyzed. These samples should serve as better proficiency testing and/or control materials than freeze-dried samples.

Two "independent" methods are being used to certify approximately 35 PCB congeners and 14 chlorinated pesticides. The first method involves a Soxhlet extraction using methylene chloride, followed by removal of the majority of the lipid material by gel permeation chromatography, followed by a separation of the PCB congeners from a majority of the chlorinated pesticides using a normal-phase liquid chromatography (aminopropylsilane phase), and final analysis by gas chromatography using electron capture detection. The second method involves a Soxhlet extraction using hexane/acetone (1:1 v:v), followed by a sulfuric acid treatment for removal of the majority of the lipid material, then removal of any remaining polar contaminants using silica

solid phase extraction, and final analysis by gas chromatography using mass spectrometric detection.

19. Certification of SRM 1941a, Organics in Marine Sediment

S.A. Wise, B.A. Benner, Jr., M.J. Hays, R.R. Rebbert, and M.M. Schantz

In 1989 Standard Reference Material (SRM) 1941, Organics in Marine Sediment, was issued with NIST assigned concentrations for trace level organic contaminants including selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides. This was the first in a series of SRMs of marine related matrices that were prepared at the request of the National Oceanic and Atmospheric Administration in support of marine pollution monitoring programs. SRM 1941 has found widespread use in the marine monitoring programs, and as a result the supplies of SRM 1941 will be depleted early in 1993. In August 1991 a new sediment material was collected at the same Baltimore harbor location as the material used for SRM 1941. The sediment material was freeze-dried and then sieved to obtain the 150 to 250 μm particle size fraction for use as SRM 1941a. Based on current usage of SRM 1941, the new batch of SRM 1941a should be sufficient for the next 5-7 years.

The original SRM 1941 has certified concentrations for 11 PAHs and noncertified concentrations for 24 additional PAHs, 15 PCB congeners, and 7 chlorinated pesticides. Since SRM 1941 was issued, we have implemented analytical procedures that will allow us to provide certified concentrations for additional PAHs. For the measurement of the PAHs in SRM 1941a, we have used two different analytical techniques: reversed-phase liquid chromatography (LC) with fluorescence detection and gas chromatography-mass spectrometric detection (GC-MS). For the GC-MS analyses we have used two different stationary phases with different selectivity for the separation of PAHs, i.e., a nonpolar phase (5% phenylmethylpolysiloxane) and a smectic liquid crystalline phase. The nonpolar phase is the typical phase used for GC separations of PAHs, whereas the liquid crystalline phase provides enhanced separation of PAH isomers based somewhat on the shape (relative positioning of the aromatic rings) of the PAH solutes. Reversed-phase LC with fluorescence detection has typically been used to measure 10-12 PAHs, whereas GC-MS can readily measure 30-40 PAHs. Therefore, the number of PAHs for which we have two independent results for use in the determination of "certified" concentrations has been limited by the LC analyses. However, by isolating specific PAH isomer fractions using normal-phase LC and then analyzing these fractions by reversed-phase LC to separate the isomers, approximately 10 additional PAHs can be measured to provide results for comparison with the GC-MS results. Using the combination of these three techniques, over 40 PAHs have been measured in SRM 1941a which will result in certified concentrations for about 20 PAHs.

For the measurement of PCB congeners and chlorinated pesticides in environmental samples, we are using GC with electron capture detection on two columns with different selectivity and GC-MS. This approach will be used to quantify approximately 20 PCB congeners and 10-15

chlorinated pesticides in SRM 1941a. In addition to measurement of PAHs, PCBs, and pesticides as in SRM 1941, we have also measured approximately 20 aliphatic carbons (n-alkanes, pristane, and phytane). The addition of aliphatic hydrocarbon data for SRM 1941a will extend the usefulness of this material to studies associated with the assessment of petroleum contamination in the marine environment.

20. Development of a Quantitative Supercritical Fluid Extraction (SFE) Method for Use in the Certification of a Diesel Fuel on Soil Standard Reference Material (SRM)

A.P. Emery and S.N. Chesler

Our group's effort to explore new automatable analytical methods has resulted in the development of a quantitative SFE method for the recovery of fuel hydrocarbons from soil samples using carbon dioxide as the extractant. To verify the precision and accuracy of the SFE method, we tested the recovery of n-alkanes of C₁₄ to C₂₀ from several prepared clays and soils, as well as waste-site samples. The results obtained with the SFE method were compared with those obtained with Soxhlet extraction. Agreement between techniques was within the uncertainty of the measurements.

Our approach to the preparation of the SRM was first tested by preparing a surrogate fuel-contaminated soil material. A gravimetrically prepared solution of SRM 1624b (Distillate Fuel Oil) in methylene chloride was combined with a soil sample collected, dried and sized at NIST. Rotary evaporation of the mixture removed the solvent and simulated surface aging found in contaminated soils. The material was extracted using both Soxhlet and NIST SFE extraction procedures.

Extracts were analyzed by capillary gas chromatography. Quantitation was performed using an internal standard technique and calibration solutions prepared from SRM 1624b. Analytical results using both extraction techniques were in good agreement with the gravimetric value. One paper on this work has been published (J. Chromatog. 606, 221-228 (1992)), with a second nearing completion. In FY93, we will scale up to the batch size required for the preparation of a quantity sufficient for the SRM.

Soil contamination resulting from diesel fuel spills and leaking underground storage tanks has become a national problem. The need to assure the quality of analytical measurements of fuel contaminated soils, particularly at the regulatory level of 100 µg/g, has contributed to the need for a NIST SRM for diesel fuel contaminated soil. This proposed SRM will be prepared at NIST and certified using both methylene chloride Soxhlet extraction and a supercritical carbon dioxide extraction.

C. Outputs and Interactions
(Organic Analytical Research Division)

1. Publications

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- Becker, P.R., Wise, S.A., Schantz, M.M., Koster, B.J., and Zeisler, R., "Alaska Marine Mammal Tissue Archival Project: Sample Inventory and Results of Selected Samples for Organic Compounds and Trace Elements," NISTIR 4731, National Institute of Standards and Technology, Gaithersburg, MD, 138 (1992).
- Becker, P.R., Koster, B.J., Wise, S.A., and Zeisler, R., "Biological Specimen Banking in Arctic Research: An Alaska Perspective," *Sci. Total Environ.* (in press).
- Brown Thomas, J.M., Christensen, R.G., and Rieger, R., "Determination of Glycyrrhetic Acid in Human Plasma by High Performance Liquid Chromatography," *J. Chromatogr.* 568, 232-238 (1991).
- Budzinski, H., Radke, M., Garrigues, P., Wise, S.A., Bellocq, J., and Willsch, H., "Retention Behavior of Alkylated Phenanthrenes on a Smectic Liquid Crystalline Phase: Application to Organic Geochemistry," *J. Chromatogr.* 627, 227-239 (1992).
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- Christensen R.G., "Determination of Oltipraz in Serum by High Performance Liquid Chromatography with Optical Absorbance and Mass-Spectrometric Detection," *J. Liq. Chromatogr.* (in press).
- Chuang, J.C., Wise, S.A., Cao, S., and Mumford, J.L., "Bioassay-Directed Fractionation and Chemical Characterization of One Organic Extract of Indoor Air Fine Particles from Xuan Wei, China with High Lung Cancer Mortality Rate," *Environ. Sci. Technol.* 26, 999-1004 (1992).

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- Craft, N.E. and Soares, J.H., Jr. "Relative Solubility, Stability, and Absorptivity of Lutein and Beta-Carotene in Organic Solvents," *J. Agric. Food Chem.* 40, 431-434 (1992).
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- Craft, N.E., Wise, S.A., and Soares, J.H., Jr., "Individual Carotenoid Content of SRM 1548 Total Diet and the Influence of Storage Temperature, Lyophilization, and Irradiation on Dietary Carotenoids," *J. Agric. Food Chem.* (in press).
- Duewer, D.L., Currie, L.A., Chesler, S.N., Schönberger, E., and MacCrehan, W.A., "Implementation and Characterization of a Robotic Protocol for the Extraction of Fat-Soluble Vitamins in Human Serum," in Proc. of the 10th International Symposium on Laboratory Automation and Robotics, Boston, MA (1992).
- Ellerbe, P., Tai, S.C., Christensen, R.G., Espinoza-Leniz, R., Paule, R.C., Sander, L.C., Sniegoski, L.T., Welch, M.J., and White V., E., "The Certification of Cocaine and Benzoylcegonine in Human Urine Standard Reference Material," *J. Anal. Toxicol.* 16 (13), 158-162 (1992).
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- Emery, A.P., Chesler, S.N., and MacCrehan, W.A., "Recovery of Diesel Fuel from Clays by Supercritical Fluid Extraction - Gas Chromatography," *J. Chromatogr.* 606, 221-228 (1992).
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- May, W.E., Benner, B.A., Wise, S.A., Schuetzle, D., and Lewtas, J., "Standard Reference Materials for Chemical and Biological Studies of Complex Mixtures," *Mutation Res.* 276, 11-22 (1992).
- Mitchell, G.D. and Bell, A.A., "Development of a Coulometric Method for Assessing the Concentration of Ambient Level of CO₂/Air in Gas Cylinder Mixtures," *J. Res. Natl. Inst. Stand. Technol.* 96(5), 541-550 (1991).
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- Northrop, D.M. and MacCrehan, W.A., "Sample Collection, Preparation, and Quantitation in the Micellar Electrokinetic Capillary Electrophoresis of Gunshot Residues," *J. Liq. Chromatogr.* 15, 1041-1062 (1992).
- Rebbert, R.E., Chesler, S.N., Guenther, F.R., Koster, B.J., Schantz, M.M., and Wise, S. A., "Preparation and Analysis of a River Sediment Reference Material for the Determination of Trace Organic Constituents," *Fresenius' J. Anal. Chem.* 342, 30-38 (1992).
- Rhoderick, G.C., "Development of a Gas Standard Reference Material Containing Eighteen Volatile Organic Compounds", *Fresenius'. J. Anal. Chem.* 341, 524-531 (1991).
- Sander, L.C., Parris, R.M., Wise, S.A., and Garrigues, P., "Shape Discrimination in Liquid Chromatography Using Charge Transfer Phases," *Anal. Chem.* 63, 2589-2597 (1991).
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- Schantz, M.M., Koster, B.J., Wise, S.A., and Becker, P.R., "Determination of PCBs and Chlorinated Hydrocarbons in Marine Mammal Tissues," *Sci. Total Environ.* (in press).
- Schantz, M.M., Parris, R.M., Wise, S.A., Won, H.T., and Turle, R., "Polychlorinated Biphenyl (PCB) Congeners and Chlorinated Pesticides in a Cod Liver Oil Reference Material," *Chemosphere* 24, 1687-1698 (1992).
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- Van Heukelem, L., Lewitus, A.J., Kana, T.M., and Craft, N.E., "High Performance Liquid Chromatography of Phytoplankton Pigments Using a Polymeric Reversed-Phase C₁₈ Column," *J. Phycology* (in press).
- Wise, S.A., Benner, B.A., Jr., Christensen, R.G., Koster, B.J., Kurz, J., Schantz, M.M., and Zeisler, R., "Preparation and Analysis of a Frozen Mussel Tissue Reference Material for the Determination of Trace Organic Constituents," *Environ. Sci. Tech.* 25, 1695-1704 (1991).
- Wise, S.A., Schantz, M.M., Parris, R.M., Rebbert, R.E., and Benner, B.A., Jr., "Standard Reference Materials for the Determination of Organic Contaminants in Marine Samples," *Analysis* 20(6), M57-M61 (1992).
- Wise, S.A., Koster, B.J., Langland, J.L., and Zeisler, R., "Current Activities within the National Biomonitoring Specimen Bank," *Sci. Total Environ.* (in press).
- Wise, S.A., Schantz, M.M., Koster, B.J., Demiralp, R., Mackey, E.A., Greenberg, R.R., Burow, M., Ostapczuk, P., and Lillestolen, T.I., "Development of Frozen Whale Blubber and Liver Reference Materials for the Measurements of Organic and Inorganic Contaminants," *Fresenius' J. Anal. Chem.* (in press).
- Wise, S.A., Schantz, M.M., Benner, B.A., Jr., Parris, R.M., Rebbert, R.E., Sander, L.C., Koster, B.J., Chesler, S.N., and May, W.E., "Standard Reference Materials for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples - Current Activities," *Fresenius' J. Anal. Chem.* (in press).
- Zeigler, R.G., Subar, A.F., Craft, N.E., Giske, U., Patterson, B.H., and Graubard, B.I., "Does Beta-Carotene Explain Why Reduced Cancer Risk is Associated with Vegetable and Fruit Intake?" *Cancer Research (Suppl.)* 52, 2060s-2066s (1992).

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- Zeisler, R., Koster, B.J., and Wise, S.A., "Specimen Banking at the National Institute of Standards and Technology," in Analytical Approaches as Related to Specimen Banking, (M. Rossbach, P. Ostapczuk, and J.D. Schladot, Eds.), Springer Verlag, Stuttgart, Germany, 37-49 (1992).
- Zeisler, R., Demiralp, R., Koster, B.J., Becker, P.R., Burow, M., Ostapczuk, P., and Wise, S.A., "Determination of Inorganic Constituents in Marine Mammal Tissues," *Sci. Total Environ.* (in press).
- Zhang, X., Martire, D.E., and Christensen, R.G., "Characterization of a Supercritical Fluid Chromatographic Retention Process with a Large Pressure Drop by the Temporal Average Density," *J. Chromatogr.* 603, 193-203 (1992).

2. Talks

- Benner, B., Jr., "Supercritical Fluid Extractions of Standard Reference Materials with Chlorodifluoromethane (R-22)," 4th International Symposium on Supercritical Fluid Chromatography and Supercritical Fluid Extraction, Cincinnati, OH, May 19, 1992.
- Benner, B., Jr., "Determination of Polycyclic Aromatic Hydrocarbons in Combustion Related Source Samples by Gas Chromatography with Mass Spectrometric Detection," Thirteenth International Symposium on Polynuclear Aromatic Hydrocarbons, Bordeaux, France, October 1-4, 1991.
- Choquette, S., "Real-time Optical Immunosensors," Biotechnology Research and Development Corporation, Chicago, IL, January 21, 1992.
- Choquette, S., "Fiber Optic Interferometry for Thermal Immunosensing," Biomedical Engineering Society, University of Utah, Salt Lake City, UT, October 18, 1992. Invited
- Craft, N., "Evolution of the NIST Fat-Soluble Vitamin QA Program," FLAIR Concerted Action No. 10 Commission of European Communities, Gandia, Spain, October 24, 1991. Invited
- Craft, N., "Influence of Storage Temperature, Lyophilization, and γ -Irradiation on Dietary Carotenoids," Federation of American Societies for Experimental Biology (FASEB), Anaheim, CA, April 8, 1992.

- Craft, N., "Fat-Soluble Vitamins and Carotenoids in Biological Reference Materials: Human Serum, Mixed Diet, and Infant Formula," 5th International Symposium on Biological and Environmental Reference Materials (BERM-5), Aachen, Germany, May 11 - 14, 1992.
- Craft, N., "Fat-Soluble Vitamins and Carotenoids in Biological Reference Materials: Human Serum, Mixed Diet, and Infant Formula," Bonn University, Bonn, Germany, May 20, 1992. Invited
- Emery, A., "Recovery of Environmental Analytes from Clays and Soils by Supercritical Fluid Extraction/Gas Chromatography," 4th International Symposium on Supercritical Fluid Chromatography (SFC) and Supercritical Fluid Extraction (SFE), Cincinnati, OH, May 20, 1992.
- Emery, A., "Trifluoromethane (CHF₃) for the Supercritical Fluid Extraction of Environmental Samples," 4th International Symposium on Supercritical Fluid Chromatography (SFC) and Supercritical Fluid Extraction (SFE), Cincinnati, OH, May 20, 1992.
- Emery, A., "Supercritical Fluid Extraction of Carotenoids from Foods," 4th International Symposium on Supercritical Fluid Chromatography (SFC) and Supercritical Fluid Extraction (SFE), Cincinnati, OH, May 20, 1992.
- Emery, A., "Supercritical Fluid Extraction of n-Alkanes and Polycyclic Aromatic Hydrocarbons from Clays and Soils," Thermophysics Division, Chemical Science and Technology Laboratory, NIST, Boulder, CO, June 1992. Invited
- Emery, A., "Recovery of Environmental Analytes from Clays and Soils by Supercritical Fluid Extraction/Gas Chromatography," 4th Symposium on Emerging Technologies for Hazardous Waste Management, Atlanta, GA, September 21, 1992.
- Epler, K., "Liquid Chromatographic Determination of Carotenoids in Human Serum," 18th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Anaheim, CA, October 8, 1991.
- Epler, K., "Liquid Chromatographic Determination of Carotenoids, Tocopherols, and Retinol in Human Serum and in Foods," 16th International Symposium on Column Liquid Chromatography (HPLC '92), Baltimore, MD, June 14-19, 1992.
- Locascio-Brown, L., "Using Components of the Immune System to Improve the Performance of Analytical Chemistry Methods," Department of Chemistry, James Madison University, Harrisonburg, VA, April 10, 1992. Invited

- MacCrehan, W., "Capillary Electrophoresis Separation of DNA Fragments Using a Soluble Gel Size-Exclusion Agent," 2nd Annual Frederick Conference on Capillary Electrophoresis, Frederick, MD, October 15-16, 1991.
- Margolis, S., "Measurement of Moisture in Oils," American Society for Testing and Materials Semiannual Meeting of Committee D-27, San Diego, CA, October 15, 1991. Invited
- May, W., "Analytical Techniques for Industrial Process Control," 2nd International ANATECH Meeting, Lake Lanier, GA, April 4, 1992. Invited
- May, W., "NIST: New Organizational Structure and Redirected Mission," Gordon Research Conference, New Hampton, NH, August 4, 1992. Invited
- May, W., "NIST Role in Providing Quality Assurance for Environmental Measurements," 204th American Chemical Society Meeting, Washington, DC, August 24, 1992. Invited
- May, W., "NIST Research and Standards Activities Directed Toward Air Emission Measurements," Environmental Research Consortium Meeting, Novi, MI, August 27, 1992. Invited
- Northrop, D., "Gunshot Residue Analysis Using Micellar Electrokinetic Capillary Electrophoresis," Institute of Forensic Sciences Criminal Investigation Laboratory, Dallas, Texas, November 22, 1991.
- Parris, R., "Comparison of Gas Chromatographic Methods for Determination of PCBs and Chlorinated Pesticides in Marine Reference Materials," 5th International Symposium on Biological and Environmental Reference Materials (BERM-5), Aachen, Germany, May 11-14, 1992.
- Parris, R., "NIST Standard Reference Materials for the Determination of Chlorinated Biphenyls, Chlorinated Pesticides, and Other Halogenated Compounds," 5th International Symposium on Biological and Environmental Reference Materials (BERM-5), Aachen, Germany, May 11 - 14, 1992.
- Sander, L., "Shape Recognition in Liquid Chromatography," American Chemical Society 204th National Meeting, Washington, DC, August 23-28, 1992. Invited
- Schantz, M., "Comparison of Methods for Gas Chromatographic Determination of PCBs and Chlorinated Pesticides in a Fish Oil Reference Material," 14th International Symposium on Capillary Chromatography, Baltimore, MD, May 25-29, 1992.
- Schantz, M., "Organic Analysis of Marine Mammal Tissue Specimens," American Chemical Society 204th National Meeting, Washington, DC, August 23-28, 1992.

- Welch, M., "The Analysis of Human Hair for Drugs of Abuse," Southwestern Regional Meeting of the American Chemical Society, San Antonio, TX, October 4, 1991. Invited
- Wise, S., "Standard Reference Materials for the Determination of PAHs in Environmental Samples -- Current Activities," 13th International Symposium on Polynuclear Aromatic Hydrocarbons, Bordeaux, France, October 1-4, 1991.
- Wise, S., "Determination of PAH Isomers of Molecular Weight 278 and 302 in Environmental SRMs," 13th International Symposium on Polynuclear Aromatic Hydrocarbons, Bordeaux, France, October 1-4, 1991.
- Wise, S., "National Biomonitoring Specimen Bank at NIST," Human Tissue Banking Workshop, Health and Welfare Canada, Ottawa, Canada, November 5, 1991. Invited
- Wise, S., "Trace Organic Analysis of Environmental Samples," Chemistry Department Seminar, University of North Dakota, Grand Forks, ND, November 20, 1991. Invited
- Wise, S., "Trace Organic Analysis of Environmental Samples," Chemistry Department, American University, Washington, DC, February 27, 1992. Invited
- Wise, S., "Standard Reference Materials for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples - Current Activities," 5th International Symposium on Biological and Environmental Reference Materials (BERM-5), Aachen, Germany, May 11 - 14, 1992.
- Wise, S., "Development of Frozen Whale Blubber Reference Material for the Measurement of PCB Congeners and Chlorinated Pesticides," 5th International Symposium on Biological and Environmental Reference Materials (BERM-5), Aachen, Germany, May 11 - 14, 1992.

3. Cooperative Research Development Agreements (CRADAs) and Consortia

Clinical Laboratory Work, M. Welch
College of American Pathologists (CRADA)

Feasibility of Development of SRMs for Formaldehyde and Methanol, W. Dorko
Motor Vehicle Manufacturers Association (CRADA)

Flow Injection Immunoassay for Measurement of Hormone Concentration in Serum,
L. Locascio-Brown
Paracelsian (CRADA)

Bio/Chemical Reagent Immobilization on Integrated Optic Hartman Interferometers for
Immunosensing, S. Choquette
Photonic Sensor Systems (CRADA)

Consortium for Automated Analytical Laboratory Systems, W. MacCrehan
ABC Laboratories, Inc. (CRADA)
Applied Analytical Industries, Inc. (CRADA)
BP America (CRADA)
CEM Corporation (CRADA)
Department of Energy and the National Laboratories
Digital Equipment Corporation (CRADA)
E.I. duPont de Nemours Company, Inc. (CRADA)
Eastman Kodak Company (CRADA)
Environmental Protection Agency (CRADA)
Hewlett-Packard Company (CRADA)
Occidental Chemical Corporation (CRADA)
The Perkin-Elmer Corporation (CRADA)
Union Carbide Corporation (CRADA)

4. Patent Awards and Applications

None

5. SRM Activities

SRM 968a Fat-Soluble Vitamin in Human Serum	SRM 1693a 50 ppm SO ₂ in Nitrogen
SRM 1507b 11-Nor- δ -9- Tetrahydrocannabinol-9-Carboxylic Acid in Freeze-Dried Urine	SRM 1694a 100 ppm SO ₂ in Nitrogen
SRM 1511 Multidrugs in Urine	SRM 1696a 3300 ppm SO ₂ in Nitrogen
SRM 1548 Total Diet	SRM 1804 5 ppb VOC in Nitrogen
SRM 1663a 1500 ppm SO ₂ in Nitrogen	SRM 1845 Cholesterol in Whole Egg Powder
SRM 1665b 3 ppm Propane in Nitrogen	SRM 1846 Infant Formula
SRM 1666b 10 ppm Propane in Nitrogen	SRM 1941a Organics in Marine Sediment
SRM 1667b 50 ppm Propane in Nitrogen	SRM 1945 Organics in Whale Blubber
SRM 1679 100 ppm CO in Nitrogen	SRM 1975 Diesel Particulate Extract
SRM 1681b 1000 ppm CO in Nitrogen	SRM 2381 Morphine and Codeine in Freeze-Dried Urine
SRM 1685b 250 ppm NO in Nitrogen	SRM 2382 Morphine Gluronide in Freeze- Dried Urine
SRM 1686b 500 ppm NO in Nitrogen	
SRM 1687b 1000 ppm NO in Nitrogen	SRM 2383 Carotenoids in Food

SRM 2389 Amino Acid Standard Solution
SRM 2619a 0.5% CO₂ in Nitrogen
SRM 2620a 1% CO₂ in Nitrogen
SRM 2623a 2.5% CO₂ in Nitrogen
SRM 2627a 5 ppm NO in Nitrogen
SRM 2628a 10 ppm NO in Nitrogen
SRM 2628a 20 ppm NO in Nitrogen
SRM 2631a 3000 ppm NO in Nitrogen
SRM 2636a 250 ppm CO in Nitrogen
SRM 2637a 2500 ppm CO in Nitrogen
SRM 2638a 5000 ppm CO in Nitrogen
SRM 2639a 1% CO in Nitrogen
SRM 2727 Automotive Emissions Mixture
SRM 2728 Automotive Emissions Mixture
SRM 2730 5 ppm H₂S in Nitrogen
SRM 273 120 ppm H₂S in Nitrogen
RM 8448 Drugs of Abuse in Human Hair
Segments
RM 8449 Drugs of Abuse in Powdered
Human Hair
RM 8506 Moisture in Transformer Oil
RM 8507 Moisture in Mineral Oil
RM 8508 Moisture in Methanol (50 µg/g)
RM 8509 Moisture in Methanol (100 µg/g)
RM 8510 Moisture in Methanol (400 µg/g)

6. **SRD Activities**

None

7. **Calibrations**

None

8. Committee Assignments

L.E. Locascio-Brown

CSTL Strategic Planning Committee on Biotechnology

N.E. Craft

Carotenoid Analytical Methods Committee, National Feed Ingredient Association
Steering Committee, Carotene Research Interactive Group

W.D. Dorko

ASTM on Analysis of Ambient Atmosphere
Steering Committee for Ambient Sulfur Gas Measurement Intercomparison Program,
NSF

W.A. MacCrehan

CSTL Colloquium Committee
CSTL Strategic Planning Committee on Chemical Process Technology

W.E. May

ACS Analytical Chemical Division Education Committee
EPA Toxic Substances Control Act, Interagency Testing Committee (DoC Representative)
Ford Foundation Predoctoral Fellowship Evaluation Panel
Governing Board, International Society on Polycyclic Aromatic Compounds
Interagency Committee on Human Nutrition Research
Interdepartment Minority Health/Science Careers Coordinating Committee (DoC Representative)
National Science Foundation Phase I Small Business Innovation Research Evaluation Panel
NIST African American Affirmative Employment Committee (Chairman)
NIST Senior Executive Service General Performance Review Board
Program Committee Chairman, International PAH Symposium

R.M. Parris

NIST CSTL Quality Assurance Committee
SRM Certification Total Quality Management Team
Washington Chromatography Discussion Group (Secretary)

L.C. Sander

NIST Research Advisory Committee

L.T. Sniegowski

NIST Child Care Center (Bookkeeper)

M.J. Welch

Advisor to Standards Committee of the College of American Pathologists
CSTL Strategic Planning Committee on Health/Clinical Chemistry
NCCLS Sub-Committee on Urine Drug Testing
NCCLS Sub-Committee on Cholesterol in Serum Reference Materials

E. White V

EPA Toxic Substances Control Act - Interagency Testing Committee (Doc Alternate)

S.W. Wise

CSTL Strategic Planning Committee on the Environment
American Chemical Society, Division of Analytical Chemistry, Publicity Committee,
(Chairman)
International Committee on Polycyclic Aromatic Hydrocarbons Sub-Committee on
Chromatography, (Chairman)

9. Editorships

N.E. Craft

Carotenoid News (Associate Editor)

W.E. May

Journal of Polycyclic Aromatic Compounds (Editorial Board)

S.A. Wise

Fresenius' Journal of Analytical Chemistry (Editorial Board)
Journal of Microcolumn Separations (Editorial Board)

10. Seminars

October 15, 1991

Dr. Garry Handelman, Department of Nutrition, University of California at Davis, Davis, California, "Techniques for Study of Human Carotenoid and Retinoid Metabolism."
(Division Sponsor: N.E. Craft)

November 7, 1991

Dr. Thomas J. Bruno, Thermophysics Division, Chemical Science and Technology Laboratory, Boulder, Colorado, "Industrial SFE: Process Design and Component Strategy." (Division Sponsor: W.A. MacCrehan)

December 9, 1991

Professor Dr. Erno Pungor, Institute of General and Analytical Chemistry, Technical University of Budapest, Budapest, Hungary, "Electrochemical Sensing." (Division Sponsor: L. Locascio-Brown)

January 23, 1992

Dr. John G. Dorsey, Chemistry Department, University of Cincinnati, Cincinnati, Ohio, "Retention Mechanisms of Reversed-Phase Liquid Chromatography: Partitioning Processes at Interfaces." (Division Sponsor: S.A. Wise)

February 19, 1992

Mr. Jeffrey A. Seeley, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, "Chromatography - AES for Boron-Selective Detection Lubrication Additives and Oils." (Division Sponsor: S.A. Wise)

March 18, 1992

Mr. Thomas E. Gills, Standard Reference Materials Program, Office of Measurement Services, Gaithersburg, MD, "NIST SRM Program: Past, Present and Future." (Division Sponsor: W.E. May).

March 19, 1992

Dr. David M. Bunk, Department of Chemistry, Texas A & M University, College Station, TX, "Protein Sequence Analysis by ^{252}Cf -Plasma Desorption Mass Spectrometry." (Division Sponsor: M.J. Welch)

March 20, 1992

Dr. Terry Bidleman, Department of Chemistry, The University of South Carolina, Columbia, SC "Toxaphene in Remote Ecosystems: Environmental Transformations and Analytical Problems." (Division Sponsor: S.A. Wise)

March 23, 1992

Dr. Steven H. Page, Department of Chemistry, Brigham Young University, Salt Lake City, Utah, "The Effect of Phase Behavior on Supercritical Fluid Chromatography with CO_2 -Based Mixed Mobile Phases." (Division Sponsor: S.A. Wise)

March 26, 1992

Ms. Melinda Hays, University of Cincinnati, Cincinnati, Ohio, "Biometabolites of Various Fish Species." (Division Sponsor: S.A. Wise)

March 27, 1992

Mr. Scott Ireland, Zymark Corporation, Hopkinton, MA, "Laboratory Automation: Vision of the 80's and Reality of the 90's." (Division Sponsor: W.A. MacCrehan)

April 29, 1992

Dr. Michael R. Moldover, Thermophysics Division, Chemical Science and Technology Laboratory, Gaithersburg, MD, "CFC Research in the Thermophysics Division." (Division Sponsor: W.E. May)

May 22, 1992

Dr. James W. Elkins, Climate Monitoring and Diagnostics Laboratory, NOAA, Boulder, Colorado, "Slowdown of the Atmospheric Growth Rates of CFC-11 and CFC-12: The Result of the Montreal Protocol." (Division Sponsor: W.D. Dorko)

June 5, 1992

Mr. John J. Pellegrino, Chemical Engineering Division, Chemical Science and Technology Laboratory, Gaithersburg, MD, "Selective Chemical Separations Using Membranes." (Division Sponsor: W.E. May)

June 23, 1992

Dr. William R. Kelly, Inorganic Analytical Research Division, Chemical Science and Technology Laboratory, Gaithersburg, MD, "Tracing Air Pollution with Enriched Stable Isotopes." (Division Sponsor: W.E. May)

August 17, 1992

Dr. Jerry W. King, Food Quality and Safety Research Unit, Agricultural Research Services, Peoria, Illinois, "Quantitative Supercritical Fluid Extraction of Lipids, Toxicants, and Trace Components from Plant and Animal Matrices." (Division Sponsor: W.A. MacCrehan)

August 19, 1992

Dr. M. Miral Dizdaroglu, Biotechnology Division, Chemical Science and Technology Laboratory, Gaithersburg, MD, "Mechanisms for Free Radical DNA Damage in Mammalian Chromatin." (Division Sponsor: W.E. May)

September 16, 1992

Dr. David L. Duewer, Surface and Microanalysis Science Division, Chemical Science and Technology Laboratory, Gaithersburg, MD, "A Novel Approach to Assigning Uncertainties to SRM Certified Values." (Division Sponsor: W.E. May)

September 28, 1992

Dr. Christine E. Evans, School of Chemical Sciences, University of Illinois, Urbana, Illinois, "Direct measurement of Separation Processes in Liquid Chromatography". (Division Sponsor: S.A. Wise)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

October 18-19, 1991

NIST/NCI Analytical Methods Development and QA Workshop, NIST, Gaithersburg, MD

November 8, 1991

2nd CAALS Workshop on Supercritical Fluid Extraction, NIST, Gaithersburg, MD

December 10, 1991

NOAA Quality Assurance Workshop, Beaufort, NC

VI. Process Measurements Division (836)

Gregory J. Rosasco, Chief

A. Division Overview

The Process Measurements Division develops new and improved measurement techniques, standard practices, and mathematical models required to describe and interpret the performance of laboratory and process instruments, and for analysis, control, and optimization of industrial processes. Emphasis is placed on measurement methods, standards, and data that are needed in the chemical, biochemical, and related industries, with a special emphasis on the development of on-line, and where possible, *in-situ* measurement techniques. Measurements of interest include fluid flow rate, liquid density and volume, humidity, chemical composition, pH, particle size, number density and volume fraction, velocity, temperature, dynamic pressure and other quantities important in multi-phase reacting and non-reacting process streams.

Accurate measurements for process and quality control require validation of measurement methods and calibration of instruments using techniques traceable to national standards. Therefore, **calibration services** represent a very important part of our activities with over 1000 standard tests and calibrations performed this year. These involved airspeed, fluid flowrate, humidity, liquid density, temperature, and volume measurements for a wide range of clients across the country. In a new effort to provide measurement services for transient temperature and pressure, this year we completed the construction of a gas-driven shock tube source which provides rapid step-changes of pressure and temperature. Initial test-services are expected to begin in the coming year. This development is a direct result of our research on optical diagnostic methods for temperature and species measurement.

Work on upgrading calibration services continues. One of the largest efforts is directed towards full **implementation of the new International Temperature Scale (ITS-90)** which we currently realize in the range between 84 and 1235 K. Two new facilities are being developed to implement ITS-90 below 84 K. One of these will provide efficient calibrations in the range 0.65 to 85 K and will replace an extremely antiquated system on which low temperature calibrations previously relied. Another major upgrade is underway in the area of **humidity standards**. Here the goal is extension of the measurement range down to 20 ppbv; currently we calibrate to 3 ppmv (-70 °C dewpoint temperature). This extension is required to enable the U.S. semiconductor manufacturing industry to accurately monitor water vapor, considered the most important contaminant, in process gases. We have constructed a low-frost point humidity generator that will operate over the range 20 ppbv (-100 °C dewpoint temperature) to 1000 ppmv. This year we have demonstrated successful performance of this new device at the -70 °C dewpoint. This facility will represent the only humidity measurement standard available for the sub-ppm range, and will be a very important tool for quality control in the semiconductor manufacturing industry. Similar efforts to improve accuracy and efficiency, driven by chemical process and custody transfer requirements of U.S. industry and government, are underway in

almost every area in which we provide calibration services; this is particularly true in the area of **fluid flowrate standards**. For example, the error budget for volumetric liquid flow rate recently has been reduced by a factor of 2 to $\pm 0.13\%$. An upgrade of our large airflow calibration facility to increase the flow range by a factor of 3 (to 85 m³/min) is under way. Improvements in liquid density and viscosity measurement also remain as important goals in the evolution of more accurate liquid flow calibration services.

A very significant portion of the Division's research effort is focused on the development of **sensors and transducers**. The **thermocouple** is still used widely in industry. We have completed a major effort to determine the emf values as a function of T_{90} for all the ISA letter-designated thermocouple types. This work relied on a major research effort, involving NIST and six other national laboratories, to derive more accurate values for S-type thermocouples of the emf versus T_{90} and of the temperature differences between T_{90} and T_{68} (ITS-68) in the range 630 °C to 1064 °C. The results of this international effort, coordinated and evaluated by NIST, were reported in several collaborative papers presented at the Seventh International Symposium on Temperature. Using these experimentally determined values, the T_{68} based reference functions for the other letter-designated thermocouple types (B, E, J, K, N, R, and T), as well for nine non-letter designated thermocouples, were converted mathematically to T_{90} based functions. Such reference functions and/or tables for thermocouples were prepared for: Standard Handbook for Electrical Engineers, ASHRAE Fundamentals Handbook, ASTM Standard E230, IEC Standard Publication 584-1, "Thermocouples, Part 1: Reference Tables", ASTM Standard E988, ASTM Standard (Draft E20 D-43) and ASTM Manual 12 on the Use of Thermocouples in Temperature Measurement.

The sensor-related research in the Division has had a strong emphasis on the development of **ultrathin film chemical sensors**. This year a new collaboration has been established with the Semiconductor Electronics Division (SED) of the Electronics and Electrical Engineering Laboratory (EEEL) in the area of integration of our ultrathin film technology with the silicon micromachined device technology available in SED. Multilevel structures employing thermal pixel technology for temperature control have been combined with a four-point resistivity measuring structure and an overlayer of SnO₂ to fabricate array elements. This approach combined with the addition of catalytic surface additives allows control and use of adsorption/desorption kinetics as a means of tuning the sensitivity and selectivity of individual sensing elements in the arrays. This effort represents a great leap forward toward the goal of realizing multi-element arrays of solid state devices for on-line gas sensing applications.

In recent years, as part of the DoE/NASA/Cummins Engine Co. adiabatic engine program, we have developed **thin film thermocouple** (TFTC) devices for direct monitoring of surface temperatures inside an engine. Thin film thermocouples, because of their low physical profile and robustness, are ideally suited as probes of temperature and heat flux transients in the high temperature, reactive environments characteristic of internal combustion and jet engines. Being multilayered structures, the response of TFTC devices is very non-linear with the frequency of the heat flux. This year we developed a system based on pulsed and sinusoidally modulated laser

heating which allows determination of the response function of TFTC devices over a wide-range of frequencies from 0.01 Hz (i.e. essentially DC) to over 100 kHz. This system has been used to characterize a TFTC heat flux gauge employed in the development of a prototype ceramic-lined diesel engine.

In another area of measurement technology for improved process measurements, our research on **optical measurement techniques** for applications in single and multiphase reacting flows is recognized worldwide. Characteristics of **liquid sprays and spray flames** are investigated using phase/Doppler and laser velocimetry techniques, which provide detailed data on droplet size, number density, and velocity. This year we demonstrated the use of these techniques to study the sooting characteristics, an important aspect of environmental impact, of methanol/toluene spray flames. We have also initiated a program of research on single, **levitated single droplets** which will allow, for the first time, tests of new theories for light scattering which take account of non-idealized laser sources. This work is expected to lead to improvements in the accuracy of commercial particle-sizing instruments.

As the complexity and sophistication of chemical processes increase, we find that our research needs to duplicate more closely the specialized conditions of temperature, pressure, and chemistry found at the forefront of chemical process technology. Two new **experimental facilities** with a special focus on such conditions have recently been brought on line. The first is a **high temperature materials synthesis reactor** with molecular beam sampling and mass spectrometric detection of molecules and clusters. This system provides a high degree of variability of residence time, composition, and temperature (to 1500 K) to enable study of rates for gas phase reaction and cluster growth. Optical access also is provided for radical production and species detection. Another flow reactor with special provision for optical access has been constructed in order to initiate studies of the **chemistry of supercritical water oxidation (SCWO)**. This new system uses single crystal sapphire windows with specially designed gold seals to enable measurements in the corrosive and highly reactive conditions characteristic of supercritical ($P > 22.1$ MPa and $T > 374$ °C) water. A light scattering (Rayleigh-Mie, Raman, and laser induced fluorescence) spectroscopy system has been constructed as the principal instrumental analysis approach for study of the phase behavior, chemical reactions, and metallic corrosion in SCWO reactors. This facility is complemented by a newly constructed global **kinetics and materials test reactor** capable of maintaining the conditions characteristic of supercritical water reactors and by our **high temperature, fluidized bed (FB) reactor**. A project, initiated last year, involving accelerated life-testing of structural materials (metals and ceramics) by means of FB environments containing chlorine species at elevated temperatures has expanded this year as part of a collaborative effort with EG&G Rocky Flats. The FB reactor is also a test bed for studying the pyrolysis and oxidation of solid organic particles in a joint study with Cornell University under sponsorship of the State of New York.

Computational approaches to better understand and predict the performance of complex chemical process streams, both reacting and non-reacting, continue to play an increasingly important role in the chemical process industry and in the research of the Division. The range

of computations in our research is quite large. We perform *ab initio* calculations of the thermochemistry and reaction rates for gas phase reactions in the oxidation of silane to high purity fine powder silicon dioxide. Such calculations allow reasonably accurate assessment of the reaction pathways and rates for intermediate reactions which are essentially intractable by conventional experimental techniques. In a collaborative effort with NASA, we are testing the accuracy of quantum, close-coupled scattering calculations used to predict spectral line formation as a function of temperature and pressure. These calculations have been verified experimentally. The accuracy of this fundamental theory allows confident extrapolation of spectral measurements of pressure and temperature to conditions which can not be produced (in a steady state) in the laboratory.

Molecular dynamics simulations of cluster-cluster collisions and subsequent formation of larger clusters are aiding our understanding of particle growth mechanisms in a size range which is extremely hard to characterize experimentally. Graphics based analyses are utilized extensively in this effort and also in the efforts to determine simplified chemical mechanisms which adequately represent the important rate or concentration limiting steps in complex chemical reaction schemes, for example, in the study of the incineration of chlorinated hydrocarbons or in attempts to model the mechanisms for fire suppression by halons.

Computational fluid dynamics (CFD) is finding application in a large range of our research and standards activities. CFD modelling of a rotating disk CVD processing reactor has been conducted this year with a special emphasis on the fate of particles produced in or injected into the flow. These models indicate the advantages in terms of temperature and gas-flow uniformity that can be realized from such a spinning disk reactor and allow investigation of flow stability criteria and of novel methods for controlling the growth and deposition of unwanted particle-contaminants on the vapor deposited film. CFD analysis of the gas flow structures in a jet-atomizer have been used for optimization of nozzle design in the **Supersonic Inert Gas Metal Atomization project (SIGMA)**. This approach has been transferred to an industrial partner in the SIGMA Consortium and resulted in a 40% increase in product yields from their processing system. Flow and heat transfer calculations based on CFD are now being expanded for use in testing the design of heaters and heat exchangers for supercritical water oxidation flow reactors and for modelling the performance of gas and liquid flow metering devices and instrumentation. This CFD approach, coupled with enhanced pressure and temperature measurement systems, holds promise for producing significant improvements (factors of two or more) in the accuracy of the national standards of gas flowrate.

As part of the expanded responsibilities and revised mission statement of the new National Institute of Standards and Technology, the Process Measurements Division is expanding its efforts to increase interactions with industry, and strives to develop and maintain all effective forms of technology transfer. Industrial consortia have been one of the most successful forms of technology transfer and our "Flowmeter Installation Effects" consortium continues to be highly successful and to attract new members. The NIST consortium project on "Intelligent Processing of Materials" is in its second phase with wider industry participation. Recent interactions with

a number of companies in the U.S. semiconductor manufacturing industry indicated that gas flow measurement problems are seriously affecting the competitiveness of the U.S. microelectronics industry. This year we have initiated a project under the sponsorship of SEMATECH to conduct round robin intercomparisons of mass flow controllers in order to achieve accuracies at the 0.25% level as required for reliable semiconductor processing. We also have established new collaborative efforts with several chemical and materials producers and have Cooperative Research and Development Agreements (CRADAs) in negotiation with them. These involve chemical processing and on-line measurements related to supercritical water oxidation, growth of nanostructured ceramics, and metallorganic chemical vapor deposition.

We also have utilized workshops and short courses (on precision thermometry, flow measurements, humidity, etc.) to assess measurement needs and transfer know-how to industrial and governmental users. Workshops organized this year are: a Workshop on the Measurement of Dynamic Temperature, at the 7th Symposium on Temperature, Toronto Canada, April 29, 1992; a Workshop on Federal Programs Involving Supercritical Water Oxidation, NIST Gaithersburg, July 6-7, 1992; and a SEMATECH/NIST Workshop on Chemistry of CVD Processes in Semiconductor Manufacturing, Sept. 29-30, 1992. We have also organized numerous technical sessions at meetings of the AIChE, AAAR, AVS, APS, MRS, and an international conference, the Seventh International Symposium on Temperature: Its Measurement and Control in Science and Industry, held in April 1992. This decennial conference is the definitive forum for defining temperature measurement capabilities throughout the world. Standards writing and trade organizations, and professional societies (such as ASTM, ASME, ISA, AIChE, API, AGA, GRI) continue to provide a forum for transfer of NIST technology to U.S. industry.

During the past year, outstanding accomplishments of our technical staff have been recognized with many awards. Dr. Gregory J. Rosasco was awarded the Department of Commerce Silver Medal for his application of laser spectroscopic techniques for temperature and pressure measurements. Mr. Walter J. Bowers, Jr. received the DoC Bronze Medal for his outstanding contributions to the development of standards for the optical measurement of gas temperature and pressure. Dr. Peter Huang received the NIST Measurement Service Award to recognize his efforts to provide high quality measurement services in humidity. Mr. Norman E. Mease, Mr. William G. Cleveland, Mr. J. Michael Hall, and Dr. George E. Mattingly received the Algie Lance Award for Best Paper at the 1992 Measurement Science Conference.

In FY92 the Division was organized into five Groups: Fluid Flow, High Temperature Processes, Reacting Flows, Process Sensing and Thermometry. The following pages describe the activities of these Groups, and their major accomplishments and future plans.

**B. Selected Technical Reports
(Process Measurements Division)**

1. Calibration and Test Services Performed by the Process Measurements Division

B.W. Mangum, G.E. Mattingly, and J.R. Whetstone

In the past year, the Division has provided calibration services in response to industry and government requests for metrological tasks in a wide variety of areas of temperature, humidity, fluid flow rate, air speed, liquid density and volume measurements. The specific calibration services offered to U.S. industry and other laboratories are summarized below:

<u>Service</u>	<u>Number of Items Calibrated</u>	
Fluid Flowrate	33	(23 for industry)
Volumetric Containers	103	(103 for industry)
Aerodynamic Devices	49	(31 for industry)
Reference Standard Hydrometers	57	(35 for industry)
Humidity	42	(33 for industry)
Standard Resistance Thermometers	102	(66 for industry)
Thermocouples	178	(177 for industry)
Laboratory Thermometers	529	(517 for industry)

These calibrations generally establish a traceability link between the national standards maintained at NIST and the standards of the requesting laboratories. In this way, a basis is provided for the assurance of all the measurements produced in the requester's laboratories. We also accomplish such assurance through Measurement Assurance Programs (MAPs) and in the past year a T-MAP, covering the range from Ar (83.8 K) to Zn (420 °C), was completed with the U.S. Army TMDE Support Group, Redstone Arsenal.

In addition, our capabilities, experimental techniques, and facilities used to perform these services are being upgraded, with concomitant improvements in measurement uncertainties. Activities in the thermometry area include an upgrading of the Liquid-in-Glass Thermometry Laboratory. An oil bath, with automatic temperature control for the range 100 °C to 300 °C, was put into operation, replacing two antiquated oil baths. This augmented the other two baths (water bath covering the range 0 °C to 100 °C and salt bath covering the range 300 °C to 550 °C) put into operation in FY91. With the new baths, the uncertainty of calibrations has been significantly reduced, in some temperature ranges by as much as a factor of ten. It is anticipated that the computer programs for automatic data acquisition and analysis will be completed during the first half of FY93. The low-temperature facility where calibrations currently are performed at temperatures below 84 K is extremely antiquated. We have long standing plans to replace it with a new facility. The ³He refrigerator and the ancillary equipment for this new facility have been received, and the modifications of the laboratory space in which the facility will be located were

completed near the end of FY92. Fixed-point cells for use in this apparatus will be constructed and evaluated in FY93. These will serve not only for realizing the ITS-90 but also for use in international intercomparisons of national realizations of the scale. Plans have been made whereby the low temperature end of the scale used in this apparatus will come from, and will be periodically checked against, the research and primary realization apparatus described below. Until the new facility is operational, the old low-temperature calibration system will continue to be used.

The Division's efforts in measurement of moisture in gases encompass the development of improved primary measurement standards. Currently calibrations are performed using humidity generators that cover the concentration range of 3 ppm_v (-70 °C dewpoint temperature) to normal atmospheric levels (60 °C dewpoint temperature). Methods are under development to extend this range to concentration levels of 20 ppb_v. These are pursued in response to the needs of the semiconductor manufacturing industry for high purity processing gases. The initial effort has been to construct a low-frost point humidity generator that will operate over the range 20 ppb_v (-100 °C dewpoint temperature) to 1000 ppm_v (-20 °C dewpoint temperature). This year the capabilities of this device have been demonstrated to dewpoint temperatures of -70 °C. A new gravimetric hygrometer also is under construction with the goal of characterizing the low-frost point humidity generator. This will constitute a major extension of NIST's capability to disseminate measurement standards for moisture concentration in gases to the 20 ppb_v level. Enhancements of other calibration facilities are discussed in Technical Reports below.

2. Flow Measurement Projects for the Department of Defense

G.E. Mattingly, G.P. Baumgarten, W.G. Cleveland, N.E. Mease, and J.F. Houser

We continue to work on several projects to respond to specific, expressed metrology needs for various Department of Defense flow measurement systems. For the Navy, this work involves characterization of a specially produced, commercial liquid flow measurement facility which is intended to have accuracies at the level of $\pm 0.025\%$. These high accuracy levels are deemed necessary by the Navy to improve their engine performance testing capability. Liquid flow measurement accuracy at this level would be about four times better than the current NIST levels of $\pm 0.13\%$. Thus, this program should significantly advance the state-of-the-art in liquid flow rate measurement. To date, this facility has been installed in an appropriate laboratory space and is operating at an accuracy level of about $\pm 0.1\%$. Improvements continue to be made to advance the performance level of this facility by improving the capabilities of its component systems and by upgrading the software which produces its results. In support of this project, we also are improving the accuracy of NIST's capabilities in liquid density measurement.

In another effort for the Navy we have characterized portable, flow-measurement transfer standards for liquids. These are intended for use in calibrating permanently installed shipboard flow instrumentation in dockside tests. The standards, acoustic-type devices, were tested in

widely ranging conditions in both ideal and non-ideal installations. Results show that in ideal installation conditions this transfer standard conforms to the $\pm 0.5\%$ accuracy specification of the manufacturer. In conditions where the unit is installed in non-ideal situations, such as near elbows, inaccuracy levels increase to $\pm 17\%$. This project has benefitted considerably from the laser-based pipeflow measurement program described below. Navy metrologists from different installations across the U.S. are joining in this work, and we expect the reported results from these tests to form the basis for Navy flow standards being written for these devices.

3. Flowmeter Installation Effects

T.T. Yeh, G.E. Mattingly, B.L. Shomaker, and J.M. Allingham

The increasing value of fluid products such as chemicals and fuels has produced wide-spread needs for improved flow measurements. Improved metering needs involve: (1) adding flowmeters to systems where previously they were not considered necessary or where measurements were not feasible; (2) increasing the accuracy of installed meters; or (3) replacing installed meters with more accurate devices. Where flowmeters are being retrofitted into systems not designed for "ideal" flowmetering conditions, or where increased levels of accuracy are desired for existing meters, the currently available standards and specifications give little or no guidance to attain desired levels of performance. This problem is addressed in our pipeflow measurement program that is in its seventh year. The program is supported by an industry-government consortium which includes flowmeter manufacturers and users - both U.S. and foreign.

This research program uses Laser Doppler Velocimetry (LDV) in a water flow facility to characterize pipeflows downstream of selected piping configurations known to disturb flowmeter performance. The configurations investigated to date have included the single elbow, two arrangements of the double elbows-out-of-plane configuration, several flow conditioners and the reducer. Recently, we have focused on the 45° elbow because of reports that it caused more disturbance to orifice and turbine meter performance than the 90° elbow. Our results show these reports to be false for a wide range of orifice meters and for the specific turbine meter design used in our program.

The results of this program include: (1) a fundamental, fluid mechanical understanding of these non-ideal pipeflows, (2) strategies to improve fluid flowrate measurements that impact industrial productivity and competitiveness - both domestically and internationally; (3) direct input into the new American metering standards being written for flowmeter installation effects; and (4) data for validation of computational models to describe and understand pipeflow phenomena. This program involves collaborative interactions with the flow measurement research program underway at NIST-Boulder.

4. Studies of the Control of Turbulent Boundary Layers Using Compliant Surfaces

D.E. Hess, W.H. Schwarz (Johns Hopkins Univ.), and G.E. Mattingly

A new research program has been initiated to assess the feasibility of controlling turbulent boundary layers. Recent research into the mechanics of turbulent boundary layers (TBL) adjacent to a rigid wall has led to the conclusion that organized (coherent) flow structures, present at random times in the buffer layer portion of the TBL, account for an inordinately large contribution to the overall Reynolds stresses. These in turn are responsible for the drag exerted by the fluid on the solid surface. Current attempts at drag reduction are focusing on the disruption and suppression of these critical flow structures. One very interesting approach exploits the idea of a flexible, but damped, boundary adjacent to the flow field. The goal is to transfer energy from the fluid into the soft-pliable solid and weaken the flow structure. This should reduce the Reynolds stresses impinging upon the boundary and thereby reduce drag. Unfortunately, the complexity of the interaction and the propensity for hydroelastic instabilities to form at the solid-fluid interface, which disrupt the flow field and increase drag, have long hampered efforts to implement this highly attractive concept.

Recently, theoretical and experimental efforts have concentrated on designing a compliant material which responds with stable motions of small amplitude, thus avoiding the large amplitude instabilities that have characterized previous studies. Such a passive compliant material has been produced. Our initial measurements of surface displacement and of the streamwise component of velocity in the boundary layer indicate that the passive compliant surface is responding to and altering the passage of individual turbulence-producing flow structures. However, to assess the effect that the flexible surface has on shear stresses in the TBL, and hence its suitability for drag reduction, simultaneous measurements of both streamwise and normal components of velocity must be correlated with the measured surface displacement.

This past year, we have completed a system to allow these critical measurements to be obtained. The specific measurements provided are the displacement of the compliant surface, acquired using a noninvasive laser-based optical technique, and the streamwise and normal components of velocity, u and v . These measurements can be made with high spatial and angular resolution at various locations in the boundary layer, just above the point for which the displacement is measured. The system is installed in the NIST 0.6 m diameter Low Turbulence Water Tunnel Facility. Three time series, sampled simultaneously, are subjected to long-time averaging procedures to obtain moments, correlations, spectral densities and probability density functions. Of particular interest are local averaging techniques such as the variable interval time average and the uv-quadrant methods. These data illustrate the relationship between the passage of a turbulence-producing flow structure above the wall and its resulting substantial local effects on the compliant substrate.

The practical applications of this research can occur in energy conservation strategies for transportation systems: it has been estimated that reducing skin friction drag can account for savings of over one billion dollar per year in fuel costs in the U.S. alone.

5. Gas Flow Traceability for the U.S. Semiconductor Processing Industries

G.E. Mattingly, G.P. Baumgarten, W.G. Cleveland, and J.M. Allingham

A round robin gas flow measurement program has been initiated to resolve industry-reported discrepancies in the results from calibration facilities used for the semiconductor producing industries in the U.S. This program, funded by SEMATECH, involves the design of a flow meter artifact and test procedure that are capable of assessing and quantifying the dynamic performance of gas flow calibration facilities. The initial phase of the program addresses a central sub-interval (200-600 standard cubic centimeters per minute (SCCM)) of the very wide flow rate range (10 SCCM to 50 standard liters per minute) that SEMATECH wishes to cover. Subsequent phases of the current program will address the remaining sub-intervals.

The artifact package has been designed to include two tandem arrangements of critical flow devices. These devices have been individually characterized at NIST using the national standards facilities for gas flow. Two different gases have been used to confirm the reproducibility of the non-dimensionalized performances of these meters. The meters have also been tested in the tandem configurations using nitrogen gas, the medium selected for the round robin program. A preliminary round robin testing program has been conducted among a selected group of SEMATECH member companies which manufacture flow meters and have calibration laboratories. The preliminary round robin results are being used to alter and improve both the artifact and test procedures. The full round robin tests are planned to be completed by the early spring of 1993. Successive phases of the program are expected to follow.

6. Supersonic Inert-Gas Metal Atomization (SIGMA)

**P.I. Espina, G.E. Mattingly, F.S. Biancaniello (MSEL), S. Osella (MEL),
S.D. Ridder (MSEL), and T.V. Vorburger (MEL)**

We continue to participate in a project on Supersonic Inert-Gas Metal Atomization (SIGMA), supported by an industry-government consortium. The objective of this project is to develop a phenomenological model and on-line measurement techniques which can be used with expert systems to control this metal powder atomization process.

Our approach relies on the research strategy of adapting increasingly more sophisticated computational fluid dynamics (CFD) techniques to model the gas flow processes and phenomena, which are also investigated using both optical and intrusive techniques. Optical techniques

include shadowgraphy, Schlieren and holographic studies of the gas-only flow. The CFD and experimental studies indicate that this powder production process is an extremely rapid and complex one, where the gas stream breaks up the liquid jet in a highly dynamic manner. The liquid droplet formation process occurs through a series of stages and ultimately produces the small droplets which are rapidly solidified to achieve the required micro-structure.

In the past year CFD studies have conclusively shown that undesirable gas-flow separation can occur for certain atomization conditions and, as a result, both the product quality and the process control are degraded. Future atomization productivity will benefit by avoiding these conditions. Results of this type, derived from both CFD and experimentation, are successfully being transferred to the member companies. The consortium members in this program have made very effective use of these CFD capabilities; process yields have been reported to increase by 40% according to one member company. The SIGMA process is industrially attractive because of its efficiency in producing metal powders with unique micro-structural properties. Such powders enable critical components such as turbine blades, valves, bearings, etc., to have improved strength and corrosion resistant properties.

7. Particulate and Droplet Diagnostics in Spray Flames

C. Presser, A.K. Gupta, H.G. Semerjian, and C.T. Avedisian (Cornell Univ.)

The overall objective of this project is the development and application of advanced, laser-based measurement techniques to study spray flames. The direct result of this continuing effort has been an increased fundamental understanding of two-phase reacting flows and the development of a database for validation of spray combustion models being developed by the Jet Propulsion and Los Alamos National Laboratories. The most important application is in the area of alternative and waste fuels, where their efficient utilization demands predictive correlations between the operating variables (nozzle design, swirl, and air/fuel ratio for any given fuel) and the resulting combustion characteristics, especially combustion efficiency and formation of pollutants.

During the past year, significant progress was made in several different areas. First, the effect of swirl on droplet transport processes was examined in a pressure-atomized, hollow-cone kerosene spray, which was introduced into coflowing, non-swirling and swirling air flow fields. Both experimental and theoretical (using the KIVA-II computer code) results for droplet mean diameter and velocity were compared at several spatial positions in the near field region of the swirling spray. The measured and calculated results agree well, indicating that the model predictions may serve as a tool to understand further fuel/air mixing processes. Second, droplet transport processes that occur in fuel sprays and spray flames have been examined using laser velocimetry, phase/Doppler interferometry and laser sheet beam photography. The introduction of swirl to the combustion air modifies the spray structure (due to formation of a toroidal recirculation zone), and leads to transport of smaller size droplets upstream towards the nozzle

exit. The data demonstrate the important role droplet transport plays in enhancing flame stability and combustion efficiency. In addition, the importance of measuring and evaluating time-varying information in sprays was found to be critical to the performance of spray systems. For example, gas turbine and rocket motor stability is dependent on suppression of combustor frequencies which alter the atomization characteristics of the spray. High-speed movies of the atomization process have shown that steady sprays are not uniform in time but can contain clusters of droplets. Droplet clustering may have significant ramifications in combustion applications for soot production. Time-dependent information and spectral analysis of these data were used to study observed instabilities in air-assisted sprays. The instability is thought to result from the competition between the recirculated regions developed by both the combustion and atomization air flow streams. Finally, in the area of soot formation, efforts focused on particulate emissions of waste fuels. The influence of chemical composition of the fuel on soot formation in spray flames was investigated using a light scattering/dissymmetry ratio technique to provide information on soot mean size and concentration. The study was carried out using binary mixtures of a sooting (i.e., toluene) and nonsooting (i.e., methanol) liquid. The results suggest that under certain conditions mixtures containing approximately three parts methanol to one part toluene, or a higher methanol content, can burn cleanly.

8. Destruction of Industrial-Waste Ingredients in Fluidized Beds

S.R. Charagundla, A. Maček, C.T. Avedisian (Cornell Univ.), Y.D. Chung, (Cornell Univ.), and N.R. Quick (EG&G Rocky Flats)

The primary thrust of current studies in the NIST fluidized-bed (FB) reactor is research and testing in support of national efforts toward destruction of industrial and hazardous wastes. During the past year, advances have been made in three different areas: (i) oxidative destruction of gas-phase model compounds representative of industrial hazardous wastes; (ii) pyrolysis and combustion of solid ingredients (plastics particles) of municipal solid waste; and (iii) accelerated life testing of structural materials for hazardous-waste incinerators.

Global kinetic studies of oxidative destruction efficiencies have been completed for three gaseous model compounds, propane and two chlorinated hydrocarbons, and a report was prepared. The project on pyrolysis and combustion of municipal-waste ingredients, done in cooperation with Cornell University, has also been completed. Time-resolved FTIR absorption spectra of both oxidation and pyrolysis products of solid polymethyl methacrylate (PMMA) have been obtained, resulting in elucidation of combustion and pyrolysis dynamics of polymer particles in fluidized beds. In view of the fact that the monomer MMA was the major early product of both pyrolysis and combustion of the polymer, an additional study of FB destruction kinetics of the monomer has been made. A report is in preparation.

The project on accelerated life testing of high-strength metals and ceramics in chlorine-containing FB media at elevated temperatures, done in cooperation with EG&G Rocky Flats, has been

expanded. An earlier test (in 1991) demonstrated the feasibility of using the NIST fluidized-bed reactor as a test unit for the ranking of relative corrosion/erosion resistances under highly corrosive/erosive conditions at 700 °C. A number of material samples have now been exposed at three temperatures, both inside the bed and above it. A report of the exposure-test procedure has been prepared. It is expected that the analysis of exposed material samples will yield information on long-term durability of structural materials at lower temperatures. This information is urgently needed for design and construction of new fluidized-bed incinerators.

9. Single-Droplet Diagnostics and Modeling

**J.T. Hodges, C. Presser, H.G. Semerjian, C. Megaridis (Univ. of Illinois-Chicago),
and G. Grehan (Univ. Rouen)**

Interaction of droplets and particles with gas flows presents a major research challenge in the areas of spray combustion and other multi-phase reacting flow systems. A major obstacle to the understanding of these processes is the lack of experimental data on properties of droplets and particles entrained by the gas flow: size, chemical composition, temperature, and number density. Experimental measurement of these properties yields valuable information regarding droplet dynamics, heat and mass transfer, and chemical reactivity. In particular, we need measurements of properties of multi-component droplets to gain understanding of several important processes which affect the combustion efficiency of sprays: atomization, vaporization, micro-explosions, etc. The goal of this project is the development of experimental techniques to supply the data necessary for validation of existing models that describe the behavior of single droplets and the development of new ones. This is being done by measurements on single levitated droplets.

During the current year, electromagnetically suspended particles have been observed using laser light scattering techniques as well as direct magnified imaging methods. We have the capability to generate and levitate electrically charged droplets of 30 - 150 μm diameter. High resolution measurements of elastic light scattering from the droplets are obtained using a scanned CCD camera. In a study of the sensitivity of elastic light scattering on the form of the incident electromagnetic wave, measurements have shown that significant departures from classical plane-wave scattering occur when focused laser beams (both circular and sheet beams) are used. These data are consistent with the Generalized Lorenz Mie Theory of elastic scattering by non-plane waves, developed by our collaborator G. Grehan. The results have direct implications regarding the accuracy of all droplet diagnostics which rely on laser-based elastic light scattering. Future work will address radiation pressure and coherent interference effects for droplets under multiple beam excitation.

A model of single-particle processes, including such details as internal circulation and multi-component liquid vaporization, has been developed in collaboration with the University of Illinois at Chicago. With the goal of model validation, individual droplets will be levitated under conditions of forced convection. A special electrodynamic balance and laminar flow

assembly have been designed and are being constructed to achieve a state of droplet levitation under high speed (up to 1 m/s) free stream flow. Internal mixing processes will be observed using a laser-induced fluorescence technique to give high resolution digital images of the evaporating droplet.

10. Chemistry in Supercritical-Water Flow-Reactors

G.J. Rosasco, A. Maček, J.M.H.L. Sengers (838), W.S. Hurst, W.J. Bowers, Jr., V. E. Bean, S.R. Charagundla, J.D. Allen, and M.I. Aquino-Class

Research is underway in support of the development of Supercritical Water Oxidation (SCWO) as a safe and efficient process for disposal of industrial wastes. During the past year two flow reactors have been designed and constructed: one with optical access for non-intrusive *in situ* studies and the other for determination of destruction efficiencies and global kinetic studies of wastes and waste model compounds.

The cell of the optically accessible reactor has been designed to operate up to 40 MPa and 650 °C, with flow rates from 10 to 0.01 ml/min. The cell has two windows for laser probing and, at 90 degrees, two windows for optical observation and access that provide f/1 collection efficiency for light-scattering (Raleigh, Mie, Raman, LIF) studies. A highly successful part of the design has been the development of a unique and reliable technology for sealing the sapphire windows, important since the windows will have a finite lifetime and the sealing problems have limited previous optical research in this field. The cell is maintained in a constant temperature furnace, providing a temperature-gradient-free environment for flow-reaction studies. Immediate studies will focus on the detection and stability of model compounds in water (e.g., urea, toluene, chlorobenzene, 1-1-1 trichloroethane, methylene chloride) for conditions up to supercritical. Long range plans are to investigate phase behavior, chemical reactivity, salt separation kinetics, materials performance, and reaction mechanisms and kinetics, and to develop techniques for *in situ* temperature and pressure measurements.

A flow reactor for kinetic studies is also operational. The newly acquired components include the reactor proper, 3.6 m long, made of stainless steel or Hastelloy (interchangeable) with the associated equipment (pumps, preheater, etc.); a fluidized-bed heater with temperature capability up to 700 °C; and a selective-ion analyzer. These components have been interfaced with the existing GC/MS and total-carbon analyzer systems. Trial runs have been made with 150-200 ppm of ethyl alcohol in water, with added hydrogen peroxide, exposed to supercritical conditions at several temperatures. These data will be used to validate the performance of the new system. Analogous studies will follow with other model compounds, where such data are lacking. Future plans also include studies of materials in SCWO systems.

11. Materials Synthesis in High Temperature Reacting Flows

M.R. Zachariah, D. Burgess, Jr., M.J. Carrier, E. Blaisten-Barojas (George Mason Univ.), and R.R. Fink

The overall objective of this project is to understand the dynamics of vapor-phase formation and growth of nano-phase materials in high temperature processes. The primary effort has focused on the use of gas phase combustion as an industrially promising reaction media for particle synthesis. The goals of the research effort are to develop; 1) molecular based models of gas phase and cluster dynamics, which can be used to optimize ceramic and semiconductor particle processing; 2) *in situ*, optically based measurement schemes that may have application to on-line process monitoring and control; 3) new fundamental principles of vapor-phase processing for the production of materials with novel properties.

During this past year we have used *ab initio* molecular orbital methods to determine the important steps in the oxidation of silane. The computations are used to determine both the thermochemistry and the reaction pathways and rates for intermediate species. These rates are then used in a detailed chemical kinetic model (with transport) of a hydrogen/oxygen diffusion flame doped with silane and compared with detailed experimental measurements made in this reactor. The computations and experiments have been used to determine some of the primary early steps to the nucleation and growth of clusters. In particular we have computed thermochemistry for silicon intermediates (HSiO , H_2SiO , H_3SiOH , HSiOOH and $\text{H}_2\text{Si}(\text{OH})_2$). We have determined that H_2O will be a primary donor of oxygen into silicon species and the rates and product branching ratios for these processes. In addition, structures for SiO polymers have been obtained (up to Si_4O_4) which give us a view of what the most energetically favored early nuclei look like (planar rings), as well as the potential energy curves for SiO insertion to increase the size of the ring. This approach has yielded new data that we have found difficult to obtain experimentally. Future work will be aimed at development of a first principles computational model for chemical nucleation rates based on results of the *ab initio* computations.

Another approach we have taken to obtain fundamental data not readily obtainable experimentally, is the application of molecular dynamics computations to understand the dynamics of cluster-cluster collisions under varying conditions of cluster temperature and collision energy. Cluster reactivity, energy accommodation and internal mixing of atoms throughout the newly formed clusters can be viewed in these time-series computations. The results indicate that clusters are highly reactive toward each other and that even large cluster (> 50 atoms) have sufficient surface energy to coalesce into spheres. Over the time scale of these computations (10 ps), considerable heating of the clusters occurs due to configurational stabilization. Statistics on atom mobilities show considerable mixing within the newly formed cluster. Future work is aimed at larger clusters (> 100 atoms) to determine the mechanism by which particles coagulate rather than coalesce and the distinction between surface and bulk diffusion rates.

A new laboratory containing a high temperature flow reactor facility is in the last stages of completion. This facility will allow for both the characterization of gas and cluster phase chemistry as well as the formation and deposition of nano-phase materials.

12. Numerical Modeling of Reacting Flows

R.W. Davis, E.F. Moore, D. Burgess, Jr., M.R. Zachariah, W. Grosshandler (BFRL), W. Tsang (833), W.M. Roquemore (WRDC), and L.-D. Chen (Univ. of Iowa)

Our joint numerical/experimental jet diffusion flame project with researchers at Wright Research and Development Center (WRDC) and the University of Iowa continued with another important success during the past year. The NIST numerical model was enhanced with the ability to simulate the temporal random (both frequency and amplitude) background noise entering the burner in an actual laboratory experiment. The experimentally observed selective amplification of this background noise to produce a train of shear layer vortices inside the flame surface was reproduced numerically. We are now awaiting experimental confirmation of the predicted amplification frequency.

During the past year a major effort was undertaken to develop a full two-dimensional model for flow and particle dynamics in chemical vapor deposition (CVD) reactors. The geometry chosen was an axisymmetric rotating disk reactor. Comparisons of computed temperature profiles with experimental data from Sandia National Laboratories confirmed the accuracy of the flow calculations. Parameter studies were then undertaken in order to determine the primary factors affecting flow uniformity in the vicinity of the substrate. In conformity with past numerical and experimental investigations, it was found that disk rotation is highly desirable for eliminating buoyant recirculation zones above the substrate which destroy deposition uniformity. As a means of studying contaminant motions in these reactors, particles of varying sizes were injected with the incoming flow and then individually tracked. The propensity of particles to impact and thus contaminate the substrate was correlated with particle size, injection location, and reactor conditions. For example, higher disk temperatures help reduce particle impacts through thermophoretic effects. Subjects for future work in this area include the effects of transient instabilities and violations of axisymmetry on the reactor flow, and the effects of chemical kinetics and particle growth on the contaminant motions.

During the past year a major chemical kinetic and fluid dynamic modeling effort was initiated to rate the potential replacements (chloro-fluorocarbons) for Halon 1301 (CF_3Br), the most widely used chemical extinguisher. The effort is part of a much larger program at NIST (managed by the Building and Fire Research Laboratory) sponsored by the Air Force to replace Halon 1301, a known ozone depleting chemical. Our computational approach is designed to complement the experimental screening of possible replacements. The effort involves the compilation of thermodynamic and kinetic information for stable and unstable halocarbons both

through literature search and data estimation. These data are being employed to construct a comprehensive mechanism for halocarbon pyrolysis and oxidation. The mechanism will then be applied to a variety of computational models, such as, plug flow and perfectly stirred reactors, premixed and diffusion flames. The primary objectives are to determine the chemical/thermal mechanisms of flame suppression and the relative effectiveness of some of the alternative agents being considered. We hope to develop a framework of both fundamental understanding and computational tools in order to allow for more efficient screening of alternatives in the future.

13. Development of a Dynamic Pressure and Temperature Primary Standard

V.E. Bean, W.S. Hurst, W.J. Bowers, Jr., and G.J. Rosasco

Our program to establish a national standard for the measurement of transient pressure and temperature involves two major efforts. The first is the development of a primary standard based on the fundamental properties of diatomic gas molecules and CARS measurement techniques. As part of this work, a gas sample cell with two-port optical access was designed and constructed for use from vacuum to 100 MPa and 295 to 1000 K. A new, innovative design for sealing the sapphire windows in the cell using gold gaskets was developed. The seals can be made reliably, and they are able to withstand pressure/temperature cycling to the design limits. This cell allows the static pressure scale to be transferred to the molecular standard. As part of this effort, high resolution CARS spectra were obtained for pure D_2 at pressures from 10 kPa to 3.5 MPa at 1000 K. From these measurements it became apparent that at elevated temperatures the solubility of D_2 in the iron/nickel alloy sample cell is sufficient to cause problems in maintaining composition of static gas mixtures of $D_2:X$. Further, the spectral measurements indicated that if sorbed gas is allowed to desorb (by lowering the pressure at constant temperature), the released gas is of changed chemistry. We have determined that the experiment can be done successfully if a flowing-gas sample cell is employed, and if pressure steps are confined to positive increments. A new flow cell and pressure control system has been designed for these measurements.

The second major part of this program is the development of a reference source of transient pressure and temperature for dissemination of the primary standard. The reference source is a shock tube. Obtained from the Naval Research Laboratory, it has been modified and tested to extend the pressure range, and is now operational in our laboratory. The tube is 7 meters long and is capable of generating a maximum reflected shock pressure of 20 MPa with a dwell time of the order of 4 ms. Testing of the operational characteristics of the shock tube has begun.

14. Optical Diagnostics in Chemically Reacting Flows

W.S. Hurst, W.J. Bowers, Jr., G.J. Rosasco, R.G. Joklik, S.Green (NASA Goddard), and L.A. Rahn (Sandia Nat. Lab.-Livermore)

The focus of this research is the development and validation of optical techniques for measurement of temperature, pressure, and species concentration. The techniques of principal interest are coherent anti-Stokes Raman spectroscopy (CARS) and thermally assisted laser induced fluorescence (THAF). In the CARS area, we continued tests of fundamental theory for line formation in systems such as N_2 and CO, which are widely used for diagnostic measurements. We currently are examining the importance of the collisional relaxation of the anisotropic portion of the polarizability to the observed spectrum. One collaborator, S. Green, has completed calculation of the relaxation matrix elements (which determine the spectrum) and we have developed a computational approach which, for the first time, will allow explicit inclusion of this component along with the more commonly considered isotropic portion of the polarizability. Comparison to the experimental data will be made in the coming year. We also completed measurements of the CARS spectra of dilute deuterium (10%) in nitrogen (90%) at 295 K in the pressure range of 5 kPa to 3 MPa. At low densities the line shape is well described by a hard collision model, a result not previously verified in Raman spectral lineshape studies. At high densities we observe distortion in the line shape, which could be explained by dimer formation or as a precursor of a collision-induced spectral feature. Neither of these phenomena have previously been observed in CARS spectra. The spectral changes associated with this new feature will provide new pressure-dependent information which must be considered in addition to the known pressure broadening and shifting of the spectral line. Resolution of the origin of this new spectral feature will require measurements to higher density and to higher temperatures.

Our studies of THAF in recent years have centered on the use of the fluorescence spectrum of OH to provide non-intrusive temperature measurements in combustors. The technique developed in our work has relied on the use of the ratio of the fluorescence signals associated with the electronic A-X emissions involving the vibrational (0-1) and (1-0) transitions. Work this year demonstrated that this temperature measurement approach can be extended to diffusion flames, with a calibration based on premixed flames of the same fuel. Temperature accuracy in the 5% range was achieved across the flame surface, even in the presence of soot. Absorption corrections were applied in the latter case, as well as corrections for nonresonant fluorescence associated with soot precursors. This work constitutes an important extension of the technique for use in practical applications. We also developed an experimental apparatus to allow single-shot, multichannel spectral detection. Using this new system, we have made an evaluation of an alternate temperature measurement approach based on the ratio of signals associated with the (0-1) and (1-2) vibrational transitions. The latter approach eliminates corrections for self-absorption which complicate use of the (1-0) vibrational transitions. Our preliminary evaluation suggests that a 5% (1-sigma) temperature accuracy can be achieved with 0.5 s time resolution using this new approach. A report discussing the use of OH-THAF for combustor diagnostics will soon be prepared.

15. Thin Film Chemical Sensors and Silicon Micromachined Structures

S. Semancik, R. Cavicchi, G. Poirier, J. Suehle (EEEL), and M. Gaitan (EEEL)

Tin oxide, in sintered powder form, is the active material for a number of commercially available, conductance-based, gas species sensors. Response selectivity is achieved with catalytic metal additives. This type of chemical sensor has several undesirable sensing characteristics (e.g., slow response times and hysteresis) that are attributable to diffusion of adsorbed species into the bulk sensor material. Thin film structures are under investigation in this project because they provide a means to reduce/eliminate diffusion effects, and because they rely primarily on fast surface adsorption/desorption mechanisms to improving sensor response. Additionally, they are compatible with microelectronic device fabrication techniques and have potential as sensing arrays of improved selectivity in multi-species concentration measurement of gas mixtures. Current efforts focus on potential thin film device structures, studies of surface adsorption mechanisms, and surface modification methods to enhance sensor performance. Crystalline films are a basic interest and are expected to play an important role in future development of multi-sensor arrays.

An exciting new direction has been established and vigorously pursued this year in collaboration with the Semiconductor Electronics Division (SED) of EEEL. This work integrates the ultrathin film technology developed in this group with silicon micromachining device technology available in SED, where thermal pixel arrays based on SiO_2 bridge structures have been developed using standard CMOS fabrication technology. These multi-layer structures use a SiO_2 supporting layer that is freely suspended above a pit that has been anisotropically etched in the silicon beneath it using a post-CMOS processing step. The dimensions of these suspended pads range from 50 to 100 micrometers on a side. Additional Si and SiO_2 layers are added to form heaters and temperature sensing levels allowing temperatures in excess of 700 °C to be attained. Our metal oxide, thin film expertise has been used to add successive levels that incorporate a four-point resistivity measuring structure with an overlayer of SnO_2 . Thin film deposition and characterization expertise developed in past years in this project has been used to rapidly advance prototype device development. Two generations of devices have been produced. Response characteristics of second generation devices are similar in character to that obtained on single crystals and epitaxial thin films of tin oxide.

The addition of silicon micromachining capability to this effort provides the possibility of tailoring sensor response through modification and control of the adsorption/desorption kinetics. This capability, combined with the addition of catalytic surface additives, holds excellent promise for a new generation of chemical sensing arrays. Patent applications have been submitted in the areas of gas sensors, materials processing, and fabrication of temperature-controlled micromachined structures. Issues to be addressed in the coming year include addition of on-chip signal processing and control circuitry, including addition of on-chip neural network capability for multi-component gas concentration measurement, improved sensing film fabrication methods,

and masking techniques needed to add various catalytic metal surface additives to individual sensing structures in a larger array.

Additional activities pursued this year include design, fabrication and operation of a custom scanning tunnelling microscope (STM) to be added to the analytical capabilities of the ultrathin film laboratory, mechanistic investigations of films having thicknesses of 20 to 100 Å, and metal-semiconductor contact characteristics. In the coming year STM capability will be used to study sensing structure surface morphology, investigate the dispersal of surface additives on sensing response, and study surface morphologies at elevated temperatures.

16. Plasma Processing In Semiconductor Manufacturing

**M. Sobolewski, J.R. Whetstone, R.G. Joklik, J. Olthoff (EEEL),
R. Van Brunt (EEEL), and J. Roberts (PL)**

This is a collaborative research area involving the Process Measurements Division and two other NIST laboratories, EEEL and PL. Plasma processes of interest are those used in pattern transfer processes necessary for semiconductor device fabrication. Achievement of submicron feature sizes relies solely upon the plasma etching of silicon and SiO₂. Many plasma reactors are based on radio frequency (rf) excited plasmas, along with a range of chemistries to achieve the desired pattern transfer characteristics, e.g., high aspect ratio trenches necessary in high-density dynamic random access memory cells. The objective of this work is development of improved process sensing techniques suitable to reactor control applications and a greater degree of knowledge of plasma chemistry controlling these systems. Research activities in FY92 have followed two principal directions:

- Completion of a SEMATECH-sponsored investigation of a Langmuir probe measurement system and its application as a diagnostic tool for plasma etching reactor, and
- Development of more accurate techniques for measuring rf current, voltage and power, primary operating parameters for plasma reactors.

Development of plasma diagnostic techniques and further characterization of plasma conditions in the GEC (Gaseous Electronics Conference) Reference Cell, a standard discharge cell geometry, have continued. GEC reference discharge cells, assembled and operated in several research laboratories, have been used to establish a firm basis for comparisons of plasma conditions between these laboratories: Sandia, University of Michigan, Wright-Patterson Aero-Propulsion Laboratory, Univ. of New Mexico, and NIST. Initial comparisons of current, voltage, and power measurements have been completed and published.

In addition to being used for these reproducibility studies, current and voltage measurements can be used to control plasma reactor operation. Analysis of these measurements, using models of

the electrical behavior of the plasma, yields estimates of plasma properties, e.g., sheath thicknesses, electron density and ion bombardment energies, critical to reactor operation. We have analyzed these measurements using plasma models and compared the results with optical emission and mass spectrometric measurements to test and refine these models. The automation of current and voltage measurements provides the means to monitor rapidly changing plasma conditions, e.g., the contamination or conditioning of the cell interior surfaces, the onset of plasma instabilities, perturbations induced by diagnostic probes, and the progress of etching processes. Although electrical measurements do not provide direct chemical information, and other tools are needed to fully characterize the complex reactions occurring during plasma processing, certain chemical changes in the plasma are readily detectable by their effect on the electrical properties. The results of this work were presented at the recent SPIE Microelectronics '92 symposium.

A second GEC reference cell became operational in the Division's optical diagnostics laboratory in FY92. It will be used in the coming year to expand our activities into reactive gas chemistries, using existing capabilities in both laser-induced fluorescence and optical emission measurements. Issues to be addressed in FY93 include comparison of gas phase etchant concentration profiles, with and without silicon present, and further development of diagnostic methods having potential for on-line monitoring of process parameters.

17. Self-Assembled Organic Monomolecular (SAM) Films

M.J. Tarlov, J. Newman (Evans Central, Inc.), and E. Bowden (N. Carolina St. Univ.)

Self-assembled monolayers (SAMs) formed spontaneously by the immersion of an appropriate substrate in a surfactant solution are being investigated for their potential in chemical sensing elements. SAMs, composed of alkanethiols chemisorbed on gold, are particularly attractive because they form densely packed, ordered molecular arrays where the exposed surface organic functional group can be easily controlled. Such surfaces are ideal systems for the construction and study of highly selective, molecular recognition sensors in chemical and biotechnological applications. In addition, there are many exciting possibilities for using SAMs as adhesion layers, corrosion barriers, and elements in molecular and opto-electronic devices.

Although many spectroscopic techniques have been successfully applied to characterizing SAMs for composition and structure, in many instances a mass spectrum of the surface giving direct molecular information about the monolayers would be particularly useful in studying chemical reactions of SAMs. In collaboration with John Newman of Evans Central (Minnetonka, MN), we demonstrated, for the first time, that SIMS can be used to obtain mass spectra of intact thiolate molecules from SAMs. Intense signals from molecular thiolate and Au-molecular thiolate ions were detected from a series of n-alkanethiolates adsorbed on Au. Molecular sulfonate

species were also detected from atmosphere-exposed SAMs indicating that the thiolate head group had been oxidized and that SAMs are more air sensitive than previously thought.

We have continued, in collaboration with Professor Edmond Bowden of North Carolina State University, to characterize structures comprised of cytochrome *c* strongly adsorbed to carboxylic acid-terminated SAMs of different thickness on Au. These studies are being done with electrochemical methods and x-ray photoelectron spectroscopy (XPS). This work demonstrates the utility of SAMs for immobilizing proteins to construct enzyme electrodes and practical biosensors. It allows refinement of the techniques used for characterizing such protein/SAM structures for such applications. The electrochemical techniques of cyclic voltammetry and impedance spectroscopy were used to determine that monolayer coverages of cytochrome *c* are formed in a stable, functional, electroactive state. XPS also revealed total coverage of adsorbed cytochrome *c* on all the monolayers. Reasonable agreement was found between theoretical electron transfer rates and those rates measured using both electrochemical methods. In a separate study it was demonstrated that cytochrome *c* could be covalently bound to carboxylic acid terminated SAMs using a carbodiimide linking reagent. Covalent immobilization of redox proteins is extremely useful in enhancing the long-term stability of amperometric biosensors.

18. Measurement of Polyimide Film Thermal Characteristics

K.G. Kreider, B.L. Shomaker, T. Davis (MSEL), and S. Roth (MSEL)

A consequence of reduced feature size in the manufacture of electronic devices is much larger device densities, and consequently, higher power consumption. This heat load must be dissipated by the chip's packaging system. Critical packaging system components are thin electrically insulating films used to mount the chip in the package. Because of their good thermal stability, polyimide and ceramic materials are used in these applications. Package design relies strongly on mathematical modeling of heat flow through these films. However, the thermal characteristics of these materials in thin film form may differ significantly from their bulk material values, resulting in significant differences between predicted and actual package performance. Measurement data on the thermal properties of thin films is at best sparse. The objective of this project is development of a measurement method for thin film thermal characteristics over the normal operating ranges of semiconductor device packages.

A measurement technique has been developed that integrates thin-film thermocouple technology with the production techniques used to make polyimide thin films. A multi-layer structure suitable for measurement of interlayer temperature gradients has been designed, and several films have been fabricated. Temperature gradient measurements enable the *in situ* evaluation of the polymer layer's thermal conductivity and diffusivity. This test specimen design permits one-dimensional heat transfer analysis of the test data and generation of *in situ* property analysis of the layers. Measurements were obtained on a three layer polyimide/thermocouple structure with results for film thermal properties that are less than bulk material values by approximately 50%.

This new technique can be applied to a variety polymer and ceramic materials used in semiconductor device packaging. Future efforts will focus on refinement of the method and extension to other materials.

19. Implementation of New International Temperature Scale (ITS-90)

G.W. Burns, G.T. Furukawa, R.S. Kaeser, E.R. Pfeiffer, J.A. Wise, M.J. Carrier, and B.W. Mangum

Until the new NIST facilities for realizing the ITS-90 and for calibrating customer thermometers below 83.8 K are completed, a continuing concern is the maintenance and stability of the present low-temperature scale which serves as the NIST reference for calibrations in the region 0.65 K to 83.8 K. The NIST-ITS-90 reference scale actually consists of two distinct "wire scales": a Standard Platinum Resistance Thermometer (SPRT)-based scale spanning the region 13.8 K to 83.8 K and used primarily for calibration of SPRTs, and a Rhodium Iron Resistance Thermometer (RIRT)-based scale spanning the region 0.65 K to 27.1 K and used primarily for calibration of RIRTs and GRTs. In FY92, an additional 2 SPRTs and 5 RIRTs were calibrated to serve as additional backup reference thermometers for the NIST-ITS-90 scale. The RIRTs were calibrated at 51 temperatures (double the normal number) between 1.0 K and 27.1 K since two or three of these will be used in an international intercomparison of the NIST reference scale below 27.1 K. In addition, the main SPRT and RIRT reference sensors for NIST-ITS-90 were intercompared again over their common region (13.8 K to 27.1 K) in a continuing investigation (since 1982) of the long-term stability of the RIRTs. All SPRT comparisons included measurements not only at the ITS-90 calibration points, but also at selected intermediate points, to accumulate data on the non-uniqueness of SPRT-indicated T_{90} values between the calibration points. The conversion of the low-temperature calibration facility's computer-operated control-and-data-acquisition system and the analysis and least-squares fitting programs from the antiquated Interdata minicomputer to PC operation was completed.

Since there are no systematic data on the non-uniqueness of temperature values indicated by HTSPRTs in the range 631 °C to 962 °C, and since such data are sparse also in the range 20 °C to 630 °C on SPRTs at the levels of precision that can be achieved with modern measurement equipment, precise comparison data are urgently needed to determine the limitations of the ITS-90. To determine the non-uniqueness, temperature uniformity and stability of the comparison apparatus must be at least as good as the measurement precision. For this work, two metal-block comparison apparatuses were completed this year, one for operation between about 400 °C and 1000 °C and the other between about 20 °C and 660 °C. To achieve the desired thermal uniformity and stability, multiple thermal shields are used. For the higher temperature apparatus, a sealed potassium heat pipe is the outer thermal shield. These apparatuses should be completely operational in FY93 and will be used in the future for automatic comparison calibrations.

20. Realization of ITS-90 below 84 K

M.L. Reilly, C.W. Meyer, W.E. Fogle, and B.W. Mangum

The new NIST facility for the primary realization of the ITS-90 below 25 K is nearing completion. The purpose of this facility is: (1) to realize the ITS-90 between 0.65 K and 24.5561 K, as defined, with an inaccuracy not greater than 0.1 mK; (2) to provide primary calibrations of capsule-type SPRTs and RRTs that subsequently will be used by the NIST calibration service to transfer the ITS-90 to the scientific, industrial, and governmental user community; and (3) to evaluate the scale over this same temperature range in terms of the non-uniqueness associated with the overlapping definitions of the scale in the range below 25 K, as well as the inherent performance differences of the scale-defining instruments. The realization of the ITS-90 below 25 K requires realizing 6 fixed points and developing a new instrumentation and measurement capability, particularly for vapor-pressure thermometry of ^3He and ^4He and for interpolating constant-volume gas thermometry employing either ^3He or ^4He . Neither of the latter techniques was used to realize the IPTS-68. During tests of the ^3He refrigerator in FY92, several major leaks were found in the ^3He recirculating system and they were repaired. The refrigerator was then operated at liquid- ^3He temperatures, evaluated and found to meet specifications. The refrigerator insert, which contains the interpolating constant-volume gas thermometer bulb, bulbs for vapor-pressure thermometry, and cells for fixed points, was constructed in FY92. We anticipate having the facility fully operational by the end of FY93.

The performance of the piston gage, which will be used to measure gas pressures in realizing 4 of the 6 defining fixed points below 25 K, was accurately characterized through an experiment designed to determine the ratios A_x/A_{N_2} , where A_x is the "effective area" of the piston for ^3He , ^4He , or H_2 , and A_{N_2} is the "effective area" of the piston as calibrated with N_2 . The ratios A_x/A_{N_2} were determined over the pressure range 1.4 kPa to approximately 101.3 kPa. Values of A_x were found to differ from A_{N_2} by as much as 12 ppm, which, although measureable and necessary to know, would not contribute an error in the realization of the fixed points at the 0.1 mK level of accuracy.

The accuracy of the ITS-90 below 1 K was examined this year. This was accomplished by first measuring the magnetic susceptibility of an empty copper-coil set and then measuring the temperature dependence of the susceptibility of cerous magnesium nitrate powder on the ITS-90, using this coil set. The results, in terms of a Curie-Weiss Law temperature dependence, indicate that the inconsistency at 0.65 K may be as large as 1 mK, the magnetic (thermodynamic) temperature being lower than that measured on the ITS-90. Although this is 10 times worse than desired, it is consistent with recent values obtained at PTB and is at the limit of uncertainty of the thermodynamic values used in deriving ITS-90.

21. High Temperature Thermometry Research

G.W. Burns, M.G. Scroger, G.F. Strouse, and B.W. Mangum

In this area of research, work on thermocouples (TCs) and SPRTs continued. Studies were completed on the emf stability and repeatability of Au/Pt TCs after prolonged heating near the freezing point of Ag (961.78 °C) and after rapid thermal cycling between the Ag point and 25 °C. These studies were done in order to determine the applicability of Au/Pt TCs as accurate and rugged secondary reference thermometers and as transfer standards at temperatures up to 1000 °C. Such TCs were stable to within ± 0.016 °C when heated for 1000 hours at about 965 °C, with intermittent thermal cycling. This is at least an order of magnitude improvement over the stability of currently available reference TCs (types S, R, and B), and also is at least an order of magnitude better than the stability of IPRTs at temperatures above 550 °C. The Au/Pt TCs were also reproducible to within 0.003 °C at the freezing-point temperatures of Ag and Al, even after prolonged heating (1500 hours) at temperatures in the range 540 °C to 1000 °C. This investigation, part of our efforts to develop new TCs as secondary reference thermometers and as fairly-inexpensive high-temperature transfer standards for industrial use, resulted in the determination of a new, highly accurate reference function based on the ITS-90.

Analyses of NIST determined emf- t_{90} data for types S and R TCs, over the range from -50 °C to 1070 °C, were completed. In addition, ITS-90 reference and approximate inverse functions were developed for these TC's. Additionally, more accurate values for ($t_{90} - t_{68}$) in the range 630 °C to 1064 °C were derived from the NIST data on type S TCs and from data obtained at six other national laboratories (as part of an international effort, coordinated and evaluated by NIST): IMGC (Italy), KRISS (Korea), NPL (UK), NRLM (Japan), VNIIM (Russia), and VSL (The Netherlands).

Using the new experimentally determined values for ($t_{90} - t_{68}$), the IPTS-68 based reference functions for the other letter-designated types of TC (B, E, J, K, N, and T), as well for 9 non-letter designated types of TCs, were converted mathematically to ITS-90 based functions. Such ITS-90 based reference functions and/or tables were prepared for: Standard Handbook for Electrical Engineers; ASHRAE Fundamentals Handbook; ASTM Standard E230 (covers the letter-designated TC types); IEC Standard Publication 584-1, "Thermocouples, Part 1: Reference Tables"; ASTM Standard E988 (covers W-Re types); new ASTM Standard, Draft E20 D-43 (covers non-letter designated types of TCs); and ASTM Manual 12 on the Use of Thermocouples in Temperature Measurement.

Calibrations and comparisons of HTSPRTs are continuing as part of a collaborative project with IMGC and VSL for (1) evaluation of HTSPRTs in regard to ac/dc effects, and their reproducibility and stability, and (2) evaluation of the ITS-90 with regard to non-uniqueness and subrange inconsistencies, particularly at temperatures above 420 °C. Determination of the latter limitations of the ITS-90 is necessary for establishing realistic uncertainty statements for calibrations. The plan involves the evaluation of 30 to 50 HTPRTs against all fixed points from

273.16 K to 1234.93 K and also against measurements made in highly-uniform comparison furnaces here and at IMGC.

During the latter part of FY91 and throughout FY92, measurements on customer SPRTs were made at all fixed points within the requested calibration ranges (with a few exceptions), as part of our investigation of non-uniqueness and subrange inconsistencies of the ITS-90.

An investigation of the stability of glass-encapsulated disc-type thermistors was completed. Although these discs are not quite as stable as bead-in-glass-probe types of thermistors, they are far superior in stability to non-glass-encapsulated disc types and they have the advantage that, as discs, they can be made interchangeable, a feature that beads do not have.

22. Thermometric Fixed Point Development

B.W. Mangum, E.R. Pfeiffer, G.F. Strouse, and G.W. Burns

Two new Ag freezing-point (961.78 °C) cells (Ag90-2 and Ag90-3) containing commercially-obtained 99.9999+ % pure Ag shot were evaluated this year. Melting/freezing behavior of Ag90-2 indicated that its freezing-point temperature is lower than that of our reference Ag cell (Ag79-1) by 5.8 mK. This is attributed to the presence of oxygen in the Ag of Ag90-2. Evaluation of the melting/freezing behavior of cell Ag90-3 showed it to be purer than cell Ag79-1 by the equivalent of 2.2 mK. Cell Ag90-3 is now our laboratory reference standard.

Three new Ag freezing-point cells were constructed this year using 99.9999+ % pure Ag, which came from a single lot and they are being evaluated for use as a Standard Reference Material (SRM) freezing-point standard. A study of the melting/freezing behavior of the three cells is currently in progress.

SRM 1972 (ethylene carbonate) and SRM 1973 (n-docosane) are still in the production stage. Since purification by zone refining has resulted in the breakage of many zone-refining tubes during purification, a different technique was tried. It was hoped that the new technique would solve the production problem. Unfortunately, the material produced by the new technique was not sufficiently pure for SRMs. Using cells already produced, these SRMs will be made available in the coming year.

**C. Outputs and Interactions
(Process Measurements Division)**

1. Publications

Avedisian, C.T., Presser, C., Gupta, A.K, and Semerjian, H.G., "Observations of Soot in Combustion of Methanol/Toluene Spray Flames," in Proc. of the ASME 1992 Winter Annual Meeting, Anaheim, CA (1992).

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2. Talks

Blaisten-Barojas, E., "A Molecular Dynamics Simulation of the Energy Accommodation in Collisions of Silicon Clusters," American Association for Aerosol Research Meeting, Traverse City, MI, October 7, 1991.

Blaisten-Barojas, E., "Molecular Dynamics Study of Cluster-Cluster Collisions," AIChE 1991 Annual Meeting, Los Angeles, CA, November 21, 1991.

Burns, G.W., "New Reference Function for Platinum-10% Rhodium Versus Platinum (Type S) Thermocouples Based on the ITS-90. Part I: Experimental Procedures," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.

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Burns, G.W., "Gold Versus Platinum Thermocouples: Performance Data and an ITS-90 Based Reference Function," Seventh International Symposium on Temperature, Toronto, Canada, April 30, 1992.

Burns, G.W., "Preparation of ITS-90 Based Reference and Inverse Functions for the Letter-Designated Thermocouple Types," IEC Sub-committee 65B, Working Group 5 meeting, NIST, Gaithersburg, MD, June 3, 1992. Invited

Burns, G.W., "New Reference Functions for Platinum-13% Rhodium Versus Platinum (Type R) and Platinum-30% Rhodium Versus Platinum-6% Rhodium (Type B) Thermocouples Based on the ITS-90," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.

Cavicchi, R., "Schottky-Ohmic-Schottky Conversions in Metal/Metal-Oxide Semiconductor Contacts," 1992 March Meeting of the American Physical Society, Indianapolis, IN, March 17, 1992.

- Cavicchi, R., "Epitaxial Growth of SnO_2 on Sapphire and TiO_2 ," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 13, 1991.
- Cavicchi, R., "Heteroepitaxial Growth and Properties of Semiconducting Oxide Films," 1992 March Meeting of the American Physical Society, Indianapolis, IN, March 20, 1992.
- Davis, R.W., "A Numerical/Experimental Study of the Dynamic Structures of a Buoyant Jet Diffusion Flame," Washington State University, Pullman, WA, July 22, 1992.
- Davis, R.W., "Low-Frequency Flame Oscillation of a Nitrogen-Diluted Propane Diffusion Flame: An Experimental and Numerical Study," 1991 Technical Meeting of the Eastern Section of the Combustion Institute, Ithaca, NY, October 14, 1991.
- Davis, R.W., "A Numerical/Experimental Investigation of the Dynamic Structures of a Buoyant Jet Diffusion Flame," Fourth International Conference on Numerical Combustion, St. Petersburg, FL, December 3, 1991.
- Espina, P.I., "Flow Modeling," Phase II Consortium on Intelligent Processing of Metals Powders: Second Semi-Annual Meeting, NIST, Gaithersburg, MD, September 17, 1992.
- Espina, P.I., "Flow Modeling," Phase II Consortium on Intelligent Processing of Metals Powders: First Annual Meeting, NIST, Gaithersburg, MD, March 17, 1992.
- Fogle, W.E., "A New Cryogenic Temperature Scale from 6.3 to 650 mK," Seventh International Symposium on Temperature, Toronto, Canada, May 1, 1992.
- Fogle, W.E., "The ^3He Melting Curve Thermometer as a Universal Temperature Transfer Standard," Seventh International Symposium on Temperature, Toronto, Canada, May 1, 1992.
- Fogle, W.E., "Stability of Rhodium-Iron Resistance Thermometers," Seventh International Symposium on Temperature, Toronto, Canada, May 1, 1992.
- Fogle, W.E., "ITS-90 Below 1 K: How Accurate Is It?," Seventh International Symposium on Temperature, Toronto, Canada, May 1, 1992.
- Furukawa, G.T., "Argon Triple Point Apparatus with Multiple Thermometer Wells," Seventh International Symposium on Temperature, Toronto, Canada, April 30, 1992.
- Furukawa, G.T., "Realization of The Mercury Triple Point," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.

- Hess, D.E., "Measurements of the Stable Response of a Passive Compliant Surface to Bursts in a Turbulent Boundary Layer," 45th Annual Meeting, Division of Fluid Dynamics, American Physical Society, Florida State University, Tallahassee, FL, November 22-24, 1992. Invited
- Hodges, J.T., "Image Analysis of Diesel Sprays," Society of Automotive Engineers, Off Highway and Powerplant Congress & Exposition, Milwaukee, WI, September 14, 1992.
- Huang, P.H., "Workshop on Humidity Calibration and Measurement Research," Measurement Science Conference, Anaheim, CA, January 28, 1992. Invited
- Huang, P.H., "NIST Humidity Measurement System and Calibration Standards," Eastman Kodak Co. Seminar, Rochester, NY, May 12, 1992. Invited
- Joklik, R.G., "Laser Induced Fluorescence of OH for Temperature Measurements in Flames," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.
- Joklik, R.G., "Laser Induced Fluorescence for Temperature Measurement in Reacting Flows," Materials Research Society Fall Meeting 1991, Boston, MA, December 4, 1991.
- Kaesler, R.S., "An ITS-90 Calibration Facility," 1992 NCSL Annual Workshop & Symposium, Washington, DC, August 3-6, 1992.
- Kaesler, R.S., "What's the Temperature," Philosophical Society of Washington, Washington, DC, January 10, 1992. Invited
- Kreider, K.G., "Thin Film Thermocouple Research at NIST," Instrument Society of America, Anaheim, CA, October 31, 1991. Invited
- Kreider, K.G., "pH Sensors for Nuclear Waste Repository Environments," Nuclear Regulatory Commission, Rockville, MD, March 17, 1992. Invited
- Kreider, K.G., "Thin Film Thermocouples," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.
- Lee, T., Schwarz, W.H., and Hess, D.E., "High-Speed Holography Whole-Field Flow-Induced Displacement Measurement of a Compliant Surface," 44th Annual Meeting, Division of Fluid Dynamics, American Physical Society, Arizona State University, Tempe, AZ, November 24-26, 1992.
- Maček, A., "Oxidation of Hazardous-Waste Model Compounds in a Fluidized Bed," American Institute of Chemical Engineers Annual Meeting, Los Angeles, CA, November 18, 1991.

- Maček, A., "Pyrolysis and Oxidation of PMMA Particles in Fluidized Beds," New York State Solid Waste Combustion Institute Conference, Ithaca, NY, April 23, 1992.
- Mangum, B.W., "Realization of the ITS-90 below 83.8 K at the National Institute of Standards and Technology," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.
- Mangum, B.W., "Current Status and Trends in Temperature Measurements at NIST, Cooperative Projects and New Mutual Agreement Between NIST and IMGC," Proc. of the Italy/USA Metrology Seminar, Torino, Italy, May 1992. Invited
- Mattingly, G.E., "Review of Flow Meter Installation Effects Research at NIST-G," Consortium Meeting, NIST, Gaithersburg, MD, October 8, 1991.
- Mattingly, G.E., "Improved Liquid Volume Measurements for Petroleum Applications," API-COPM Meeting, Stouffer Hotel, Crystal City, VA, October 21, 1991.
- Mattingly, G.E., "Pipe Flow Profile Measurements Downstream from a Tee and from a Reducer," ASME-MFFCC Meeting, Hyatt Hotel, Boston, MA, November 13, 1991. Invited
- Mattingly, G.E., "Fluid Mechanics Studies in Supersonic Inert Gas Metal Atomization," Dept. of Mech. Engr., Worcester Polytechnic Institute, Worcester, MA, November 14, 1991. Invited
- Mattingly, G.E., "Flow Measurement," ISA Montgomery County Region, Anchor Inn, Wheaton, MD, November 19, 1991. Invited
- Mattingly, G.E., "Round Robin Flow Measurement Programs: Theory and Practice," SEMATECH, Austin, TX, January 30, 1992. Invited
- Mattingly, G.E., "Numerical Modeling of the Gas-Only Flow in a Supersonic Inert Gas Metal Atomizer," Annual Meeting of Consortium Participants, NIST, Gaithersburg, MD, March 17, 1992.
- Mattingly, G.E., "NIST-G Water Tunnel Research," Office of Naval Research, Arlington, VA, May 1, 1992.
- Mattingly, G.E., "Flow Measurement," Measurement Technology Seminar, Sheraton-Potomac Inn, Gaithersburg, MD, May 12, 1992. Invited
- Mattingly, G.E., "Current Progress in Flowmeter Installation Effects Standards," SEMATECH, Austin, TX, May 21, 1992.

- Mattingly, G.E., "Progress Review for NIST-DoD/CCG Flow Measurement Projects U.S. Navy," David Taylor Research Center, Annapolis, MD, June 9, 1992.
- Mattingly, G.E., "An Assessment of an Ultrasonic Flowmeter in Ideal and Non-ideal Installation Conditions," NCSL Workshop and Symposium, Hyatt Hotel, Washington, DC, August 5, 1992. Invited
- Mattingly, G.E., "Flow Measurement Short Course: Meters, Calibrators, Traceabilities and Research Topics," Mexico City, Mexico, August 24-26, 1992. Invited
- Meyer, C.W., "Gas Dependence of the Effective Area of the Piston Gauge to be Used for the NIST Realization of the ITS-90," American Physical Society Meeting, Indianapolis, IN, March 18, 1992.
- Meyer, C.W., "Gas Dependence of the Effective Area of the Piston Gauge to be Used for the NIST Realization of the ITS-90," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.
- Poirier, G., "Identification of the Thermally Induced Facet Planes of $\text{TiO}_2(001)$ Rutile by STM," IBM Almaden, San Jose, CA, November 12, 1991.
- Poirier, G., "Identification of the Thermally Induced Facet Planes of $\text{TiO}_2(001)$ Rutile by STM and LEED," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 13, 1991.
- Presser, C., "Time-Based Ensemble Scattering Measurements in Fuel Sprays," 24th Fall Technical Meeting of the Eastern Section of the Combustion Institute, Ithaca, NY, October 16, 1991.
- Presser, C., "Measurement of Particle Size by Laser Diffraction During Inert Gas/Metal Powder Atomization," ASME Winter Annual Meeting, Atlanta, GA, December 2, 1991.
- Presser, C., "Aerodynamic Effects on Fuel Spray Structure-Experiment and Theory," 30th AIAA Aerospace Science Meeting and Exhibit, Reno, NV, January 6, 1992.
- Presser, C., "Estimation of Droplet Collision Frequency in a Spray," 5th Annual Conference on Liquid Atomization and Spray Systems, San Ramon, Ca, May 20, 1992.
- Reilly, M.L., "A Realization of the Triple Point of Xenon," Seventh International Symposium on Temperature, Toronto, Canada, April 30, 1992.

- Rosasco, G.J., "Simultaneous Measurement of Temperature and Pressure by means of CARS," NASA Langley Measurement Technology Conference, NASA Langley Research Center, Hampton, VA, April 23, 1992.
- Rosasco, G.J., "Q-branch Lineshape Functions for CARS Thermometry," Seventh International Symposium on Temperature, Toronto, Canada, April 28, 1992.
- Schooley, J.F., "Thermodynamic Gas Thermometry in the Range 230 °C to 660 °C," Seventh International Symposium on Temperature, Toronto, Canada, April 30, 1992.
- Semancik, S., "Metal Islands on Single Crystal SnO₂: Electrical Observation of Chemical Interactions," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 12, 1991.
- Semancik, S., "Development of Tailored Films and Surfaces for Use in Advanced Chemical Sensors," Spring '92 Meeting of the Materials Research Society, San Francisco, CA, April 29, 1992. Invited
- Semancik, S., "Microstructure-Controlled Films and Interfaces for Advanced Solid State Gas Sensors," Gordon Conference on the Chemistry and Chemical Physics of Microstructure Fabrication, Meriden, NH, July 28, 1992.
- Soulen, R.J., Jr., "A Decade of Absolute Noise Thermometry at NIST Using a Resistive SQUID," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.
- Soulen, R.J., Jr., "Noise Thermometry Based on an R-Squid Noise Thermometer," Conference on Precision Electromagnetic Measurements, Paris, June 8-12, 1992.
- Strouse, G.J., "Investigation of High-temperature Platinum Resistance Thermometers at Temperatures up to 962 °C, and in Some Cases, 1064 °C," Seventh International Symposium on Temperature, Toronto, Canada, April 28, 1992.
- Strouse, G.J., "Investigation of the ITS-90 Subrange Inconsistencies for 25.5-Ohm SPRTs," Seventh International Symposium on Temperature, Toronto, Canada, April 28, 1992.
- Strouse, G.J., "NIST Implementation and Realization of ITS-90 Over the Range of 83 K to 1235 K: Reproducibility, Stability and Uncertainties," Seventh International Symposium on Temperature, Toronto, Canada, April 29, 1992.
- Strouse, G.J., "NIST Assessment of ITS-90 Non-Uniqueness for 25.5 Ohm SPRTs at Gallium, Indium and Cadmium Fixed Points," Seventh International Symposium on Temperature, Toronto, Canada, April 30, 1992.

- Tarlov, M.J., "Reactivity of Evaporated Metals on Organosulfur Monolayers on Gold," 18th Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Anaheim, CA, October 10, 1991.
- Tarlov, M.J., "The Interaction of Evaporated Metals with Self-Assembled Alkanethiol Monolayers on Gold," American Vacuum Society, Seattle, WA, November 14, 1991.
- Tarlov, M.J., "Static Secondary Ion Mass Spectrometry of Self-Assembled Alkyl Thiol Monolayers on Gold," 204th National Meeting of the American Chemical Society, Washington, DC, August 25, 1992.
- Wise, Jacquelyn A., "Stability of Glass Encapsulated Disc Type Thermistors," Seventh International Symposium on Temperature, Toronto, Canada, April 30, 1992.
- Yeh, T.T., "NIST Consortium Research Program on Flowmeter Installation Effects," Semi-Annual Consortium Participant Meeting, NIST, Gaithersburg, MD, October 8, 1991.
- Yeh, T.T., "Research on Flowmeter Installation Effects," MRF TAC Meeting, SWRI, San Antonio, TX, April 14, 1992.
- Yeh, T.T., "Installation Effects on Flowmeters," Utilities Committee Meeting, NCSL, Washington, DC, August 4, 1992. Invited
- Zachariah, M.R., "The Importance of Detailed Kinetics in Particle Formation: Examples from the Si-O System," American Association for Aerosol Research Meeting, Traverse City, MI, October 8, 1991.
- Zachariah, M.R., "Aerosol Processing of YBaCuO Superconductors in a Flame," AIChE 1991 Annual Meeting, Los Angeles, CA, November 18, 1991.
- Zachariah, M.R., "In-Situ Measurements of Si-O Chemistry during Homogeneous Nucleation," AIChE 1991 Annual Meeting, Los Angeles, CA, November 19, 1991.
- Zachariah, M.R., "Optical Measurements for Gas Phase Diagnostics," Engineering Foundation Conferences, Kailua-Kona, HI, January 14, 1992. Invited
- Zachariah, M.R., "Chemical Kinetics and Aerosol Dynamics During Vapor Phase Formation of Ceramic Particles," George Mason University, Computational Sciences and Physics Dept., Fairfax, VA, March 20, 1992. Invited
- Zachariah, M.R., "Principles of Gas Phase Nucleation," Brown University School of Engineering, Providence, RI, April 24, 1992. Invited

Zachariah, M.R., "Principles of Gas Phase Processing of Ceramics and the Potential for Microgravity Research," 2nd International Microgravity Combustion Workshop, September 16, 1992. Invited

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Reactions in Near-Critical Water, Gregory J. Rosasco
CONOCO Inc.(CRADA)

Flowmeter Installation Effects Consortium, George E. Mattingly
Ford Motor Company
Ketema - McCrometer Division
Rosemount, Inc.
Controlotron, Inc.
Gas Research Institute
Institute of Paper Science and Technology
Chevron Oil Field Research Company
Dow Chemical U.S.A.
Kimmon Manufacturing Company, Ltd. (Japan)
E.I. DuPont de Nemours & Company
N.V. Nederlands Gasunie
Daniel Industries, Inc.
Pacific Gas & Electric Company
NOVA Husky Research Center
Instrument Testing Services

Supersonic Inert-Gas Metal Atomization, Gregory J. Rosasco
Ampal/Metallurgy
Crucible Materials Co.
DoE/Office of Industrial Processes
General Electric Aircraft Engines
Martin Marietta
United Technologies - Pratt & Whitney

4. Patent Awards and Applications

Kreider, K.G., "Intermetallic Thermocouples" (Submitted October 1991)

Semancik, S., Cavicchi, R.E., Gaitain, M., and Suehle, J., "Temperature Controlled Micromachined Arrays for Chemical Sensor Fabrication and Operation" (Submitted July 1992)

Semancik, S., Cavicchi, R.E., Suehle, J., and Gaitan, M., "Microsubstrates for Materials Processing" (Submitted July 1992)

Semancik, S., Gaitan, M., Suehle, J., and Cavicchi, R.E., "Micro-Hotplate by CMOS Technology" (Submitted September 1991)

5. SRM Activities

SRM 1972 Ethylene Carbonate Triple-point Temperature Standard (in progress)
SRM 1973 n-Docosane Triple-point Temperature Standard (in progress)
SRM 1746 Silver Freezing-point Standard (in progress)

6. SRD Activities

None

7. Calibrations

Calibration services (air speed, fluid flow rate, humidity, liquid density, temeptrature, and volume) have been provided for the following:

Accuracy Scientific Inst.	Atomic Energy of Canada Ltd
Aerospace Optics Inc.	AT&T
Air Force Arnold	Automatic Systems Labs Inc.
Air Force Griffiss	AVX Corp.
Air Force Newark	Babcock & Wilcox
Air Force Wright Patterson	Bailey Controls Co.
Aircraft Engines	Baltimore Gas & Electric Co.
Allegheny Power System	Barber Colman Co.
Allied Signal Inc.	Battelle Memorial Institute
Allison	Becton Dickinson Diagnostics
Aluminum Co of America	Becton Dickinson & Co.
Alyeska Pipeline Service Co.	Belfort Instrument
American Meter Co.	Berkeley Antibody Co Inc.
Amoco Oil Co.	Boonton Electronics Corp.
Amphenol	Brooklyn Thermometer Co Inc.
AMS Corp.	Brooks Instrument
Analytical Technologies Inc.	B&W Nuclear Technologies
Appalachian Power Co.	C Temp
Atmospheric Sciences Lab	Cal Lab

Calib Testing & Instrument Inc.
California Alloy Co.
Center for Measurement Stds.
CGS Thermodynamics
Chesapeake Laser Systems
Chevron Pipe Line Co.
CI Systems Ltd
City of Jacksonville
Cleveland Elec Illuminating Co.
Cleveland Electric Labs Co.
Climatronics Corp.
Combustion Engineering Inc.
Commonwealth Edison Co.
Conax Buffalo Corp.
Conrad Kacsik Inst Sys Inc.
Consumers Power Co.
Convectronics Inc.
Coors Brewing Co.
Corning Inc.
Cozad Instrument Co.
Crawford Long Hosp of Emory Un.
Curtin Matheson Scientific Inc.
Davis Instrument Mfg Co Inc.
Defense Procurement Div.
Detroit Edison
DHHS/Food & Drug Admin
DHHS/PHS/Food & Drug Admin
Douglas Aircraft Co.
Dow Chemical USA
Dravon Medical Inc.
DRB Industries
Duke Power Co.
Duro-Sense Corp.
E I Dupont Nemours & Co Inc.
E M Diagnostics Systems Inc.
Eastern Stainless Corp.
Eastman Kodak Co.
EG&G Automotive Research
EG&G Idaho Inc.
EG&G Inc.
EG&G Mound Applied Tech.
EG&G Rocky Flats Inc.
EG&G Rotron Inc.

Electronic Development Labs
Eli Lilly & Co.
Emerson Electric Co.
Engelhard Corp.
Engelhard West Inc.
Enzon Inc.
ETL Testing Labs Inc.
Ever Ready Thermometer Co Inc.
Exxon Co USA
Faichney Medical Co.
Fenwal electronics Inc.
Fisher Scientific
FMC Corp.
Food & Drug Administration
Ford Motor Co.
Foxboro Co.
Francis Freas Glass Works Inc.
Furnace Parts Inc.
Gage Lab Corp.
Gay Engineering & Sales Co Inc.
GE Aircraft Engines
GE Computer Service
General Dynamics
General Eastern Instruments
General Electric Co.
General Measurements Co Inc.
Gibraltar Biological Labs Inc.
Giddings & Lewis
Gordon Co.
Gossman Instrument Svc.
Gulf States Utilities Co.
H B Instrument Co.
Hall Brothers Mfg Co.
Hanna Instruments Inc.
Hart Scientific
Herguth Labs Inc.
Hill Top Biolabs Inc.
Hoechst Celanese
Hoskins Mfg Co.
Howmet Corp.
Humonics Inc.
Huntsman Chemical Corp.
IBM Corp.

IFR Systems Inc.
Indiana Michigan Power Co.
Industronics Service Co.
Instrulab
Instrument Lab.
Instrument & Control Systems
Intech Automation Sys Corp.
Iowa-Illinois Gas & Electric
Jim Beam Brands Co.
John Fluke Mfg Co Inc.
Johnson Controls World Svcs.
Johnson Gage & Inspection Inc.
Johnson Matthey
Joliet Metallurgical Labs Inc.
Jorgensen Forge
Kahn Co.
Kaman Aerospace Corp.
Kaydon Ring & Seal Inc.
Kayness Inc.
Kelley Completion Svcs Inc.
Klock
Kulas Systems
Kurz Instruments Inc.
L S Starrett Co.
Leeds & Northrup Metallurgical
Lewis Electronics Inst.
Linacre Labs
Lockheed Advanced Devel Co.
Lockheed Aeronautical Sys Co.
Lockheed Missiles & Space Co.
Magnavox Electronic Systems Co.
Marlin Mfg Corp.
Martin Marietta Astronautics
Martin Marietta Energy Sys Inc.
Massachusetts Inst of Tech.
McDonnell Douglas Aircraft Co.
McDonnell Douglas Corp.
McNeil Pharmaceutical
MD Instruments Inc.
Melcam Standards Lab
Meter Engineers Inc.
Middlesex Water Co.
Miles Inc.

Miller & Weber Inc.
MKS Instruments Inc.
Mobil Oil Corp.
Multi-Amp Corp.
MVM Enterprises
NASA Ames Research Ctr
NASA Langley Research Ctr
National Semiconductor Corp.
Naval Air Warfare Center
Naval Weapons Center
Navy Primary Stds Lab East
Navy Primary Stds Lab West
Nelson Instrument Svc Co Inc.
Nelson Jameson Inc.
Northrop Corp.
Northwest Research Assoc Inc.
NYS College of Ceramics
Oliver B Cannon & Son Inc.
Omega Engineering Inc.
Ontario Hydro Service Centre
Ortho Pharmaceutical Corp.
Palmer Instruments Inc.
Pan Am World Services Inc.
Paramax Systems Corp.
PCC Airfoils Inc.
Pemberton Fabricators Inc.
Pemco Aeroplex Inc.
Pennsylvania Power & Light Co.
Perry Equipment Corp.
PGP Industries Inc.
Philadelphia Electric Co Labs
Plantation Pipe Line Co.
PMC Corp.
PPG Industries
Pratt & Whitney
Precision Scientific
Process Instruments Inc.
Projects Inc.
PSE&G Co.
PSE&G Research & Testing Lab
Public Health Lab
Pyco Inc.
Pyromation Inc.

Pyrometric Service Co Inc.
QC Inc.
Qualimetrics Inc.
Ram Sensors
Raytheon Co.
RDF Corp.
RM Young Co.
Rockwell International
RP Services
Ruska Instrument Corp.
S African Science & Tech.
Sanata Barbara Infrared Inc.
Sandelius Instruments Inc.
Sandia National Labs
Saudia Arabian Airlines
Schott Glass Technologies
Scientific & Commercial Sys.
Sensing Devices Inc.
Service Associated Inc.
Sethness Products Co.
SGS Control Services
SGS RFGM
SGS Thomson
Shell Oil Co.
Sherwood Medical
Signetics Co.
Simco Electronics
Smith Systems
South Carolina Electric & Gas
Southwest Research Institute
Southwest Sciences Inc.
Special Metals Corp.
Spectrodyne Inc.
Sper Scientific Ltd
SSC Lab
St Jude Medical Inc.
Stabro Labs Inc.
Stanford University
State of Arkansas
State of Louisiana
Stillings Instrument Sys Co.
Tampa Electric Co.
Teledyne Geotech

Teledyne Hastings-Raydist
Tennessee Valley Authority
Teradyne Inc.
Textron Defense Systems
Thermal Science Inc.
Thermal Electric Co Inc.
Thermo Temp Instruments Inc.
Thiokol Corp.
Tobacco Institute Testing Lab
Transmation Inc.
TRW Inc.
TRW Space & Defense Sector
TSI Inc.
Tu Electric
Tudor Technology Inc.
Unified Industries Inc.
Unisys Corp.
Univ Corp for Atmospheric Res.
Univ of California
Univ of Maine
US Army TMDE Activity
US Department of Commerce
US Dept of Labor
US Dept of the Interior
US Geological Survey
Vaisala Inc.
Valley Heat Treat Co.
Veeco Instruments Inc.
Velcro Group Corp.
Victory Engineering Corp.
Vishay Foil Resistors
Wadsworth/Alert Labs
Washington Public Power Supp.
Wavetek
Westinghouse Electric Corp.
Westinghouse Hanford Co.
Westinghouse Savannah River Co.
Wiltec Research Co Inc.
WL Walker Co Inc.
Wyeth-Ayerst Labs
York International Corp.

8. Committee Assignments

D.R. Burgess

SEMATECH/NIST Workshop on CVD Chemistry, Organizing Committee

G.W. Burns

ASTM E-20 Committee on Temperature Measurement

ASTM Subcommittee E-20.04, Thermocouples

ASTM Subcommittee E-20.94, Publications

Instrument Society of American SP-1.1, Committee on Temperature Measurement
(Thermocouples)

Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee

R.W. Davis

Combustion Institute 24th Symposium (International) on Combustion, Technical Program
Committee

W.E. Fogle

Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee

G. Furukawa

Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee

J.F. Houser

ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers

R.S. Kaeser

Philosophical Society of Washington (Treasurer)

K.G. Kreider

ASTM E20 Committee on Temperature Measurement
ASTM E20.04 Subcommittee on Thermocouples
IEEE Technical Committee on Sensor Standards, TC-9 (Chairman)

G.E. Mattingly

ASME Main Committee on the Measurement of Fluid Flow in Closed Conduits
ASME SC-2 Subcommittee on Pressure Differential Devices
ASME SC-6 Subcommittee on Glossary of Terms for Flow Measurements
ASME SC-14 Subcommittee on Measurement of Fluid Flow Using Gravimetric and Volumetric Techniques (Chairman)
ASME SC-15 Subcommittee on Installation Effects on Flowmeters
ASME SC-16 Subcommittee on Vortex Shedding Type Flowmeters
ASME Main Research Committee on Fluid Meters
ASME SC-11 Subcommittee on Test Methods and Calculation Procedures (Chairman)
International District Heating Association: Testing Heat Meters Used in Fluid HVAC Systems
International Measurement Congress (IMEKO) Technical Committee No. 9 - Flow Measurement
Technical Advisory Committee for the GRI Sponsored Flow Metering Research Program at Southwest Research Institute

B.W. Mangum

ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.03, Resistance Thermometers
ASTM Subcommittee E20.06, New Thermometers and Techniques (Chairman)
ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.08, Medical Thermometry
Working Group WG.02, Fever Thermometers
Working Group WG.02A, Electronic Fever Thermometers
Working Group WG.02C, Disposable Fever Thermometers
Working Group WG.03, Continuous Clinical Temperature Monitoring Systems
Working Group WG.04, Clinical Laboratory Temperature Measurement
ASTM Subcommittee E-20.90, Executive Subcommittee
Comité Consultatif de Thermométrie (of the CIPM) Delegate)
International Electrotechnical Commission, (IEC) TC65/SC65B/WG5, Industrial Process Measurement and Control/Devices/Temperature Sensors (Chairman of WG5)
National Conference of Standards Laboratories, Ad Hoc Committee 91.3 on The Change of the Temperature Scale (Chairman)
Seventh International Symposium on Temperature, Its Measurement and Control in Science and Industry, Program Committee

E.R. Pfeiffer

ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.03, Resistance Thermometers
ASTM Subcommittee E-20.06, New Thermometers and Techniques
ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.08, Medical Thermometry
Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee

C. Presser

ASME K6-Committee on Heat Transfer in Energy Systems
Admissions committee of Sigma Xi - NIST Chapter
ASTM Subcommittee E29.03 on Int'l Cooperation on Terminology, Standards and
Methods of Particle Size Measurements
ASTM Subcommittee E29.04 on Liquid Particle Measurements, Committee E29 on
Particle Size Measurements
Chairman of the ASTM Subcommittee E29.05 on Reference Materials, Committee E29
on Particle Size Measurements
Member of the AIAA Nat'l Energy Terrestrial Systems Technical Committee

M.L. Reilly

ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.02, Radiation Thermometry Working Group E-20.02.01, Test
Methods (Chairman)
ASTM Subcommittee E-20.06, New Thermometers and Techniques
ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.91, Editorial and Nomenclature
Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee

G.J. Rosasco

Combustion Institute - 24th Symposium (International) on Combustion, Program
Subcommittee
Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee

J.F. Schooley

Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Program Committee (Chairman)

S. Semancik

American Vacuum Society, Thin Film Division, Program Committee

J.R. Whetstone

ISA Standards and Practices, Board of Directors
SEMATECH/NIST Workshop on CVD Chemistry, Organizing Committee

J.A. Wise

ASTM E-20 Committee on Temperature Measurement (Chairman)
ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers
(Secretary)
ASTM Subcommittee E-20.08, Medical Thermometry
ASTM Subcommittee E-20.90, Executive Subcommittee (Chairman)
ASTM Subcommittee E-20.91, Editorial and Nomenclature (Secretary)

M.R. Zachariah

Combustion Institute - 24th Symposium (International) on Combustion, Program
Subcommittee
AAAR Aerosol Technology Group (Chairman)
AIChE Material Engineering & Science, Area 8d. - Ceramics
SEMATECH/NIST Workshop on CVD Chemistry, Organizing Committee

9. Editorships

J.F. Schooley

Seventh International Symposium on Temperature, Its Measurement and Control in
Science and Industry, Vol. 6 (Editor)

G.E. Mattingly

International Journal of Flow Measurement and Instrumentation (North American Editor)

C. Presser

Proc. of session published in Air Toxic Reduction and Combustion Modeling, FACT-Vol.
15, Amer. Soc. Mech. Eng., NY. 1992.
Proc. of session published in General Papers in Heat Transfer and Heat Transfer in
Hazardous Waste Processing, HTD-Vol. 212, Amer. Soc. Mech. Eng., NY.
1992.

10. Seminars

October 4, 1991

Evan Whitby, Hitachi Corporation, Japan, "Simulation of Particle Dynamics in Chemical
Vapor Deposition Reactors: Development of CONTAMINATE, Version 1.0."
(Division Sponsor: M.R. Zachariah)

January 8, 1992

Kevin A. Davis, Princeton University, Department of Mechanical Aerodynamics Engineering, "Gas Phase Combustion Synthesis of Refractory Materials." (Division Sponsor: M.R. Zachariah)

February 5, 1992

Professor Ugo Piomelli, University of Maryland, College Park, MD, "Numerical Solution of the Viscous Flow in an Atomization Die." (Division Sponsor: P.I. Espina)

February 26, 1992

Mr. Paul Papas, Princeton University, "An Additive Approach to Supersonic Combustion." (Division Sponsor: D.R.F. Burgess)

March 27, 1992

Stephanie Bell, National Physical Laboratory, United Kingdom, "The UK Humidity Standard." (Division Sponsor: P.H. Huang)

April 1, 1992

Dr. Shmuel Eidelman, Science Applications International Corporation, McLean, VA, "Numerical Simulation of the Multi-Phase Time Dependent Reactive Flows with Shock Waves." (Division Sponsor: C. Presser)

April 22, 1992

Jorma Jokiniemi, Technical Research Centre, Finland, "Modeling Efforts of Aerosol-Vapor Dynamics at VTT's Aerosol Technology Group." (Division Sponsor: M.R. Zachariah)

May 13, 1992

W.L. Tew, BIPM, France, "Temperature Coefficients of Inductance in Bulk Superconducting Circuits and Their Effects on Cryogenic Electric Reference." (Division Sponsor: B.W. Mangum)

May 6, 1992

Dr. Lynn Melton, University of Texas, "Fluorescent Diagnostics for Droplets, Fuel Sprays, Gaseous Jets, and Flames." (Division Sponsor: G.J. Rosasco)

May 14, 1992

R.P. Robertazzi, IBM, T.J. Watson Research Center, Yorktown Heights, NY 10598, "High Tc Josephson Junctions." (Division Sponsor: B.W. Mangum)

June 16, 1992

Dean Verhoeven, Institut Francais de Petrole, Rueil Malmaison, France, "Holographic, Interferometric, Optical Tomography." (Division Sponsor: J.T. Hodges)

June 19, 1992

Dale Berkley, Naval Research Laboratory, Washington, DC, "Pressure Dependence of the Superconducting Transition Temperature in High T_c Superconductors up to 7 GPa." (Division Sponsor: B.W. Mangum)

June 24, 1992

Mark E. Filipkowski, Naval Research Laboratory, Washington, DC, "Temperature Dependence of the 90° Interlayer Exchange Coupling in Fe/Al/Fe(001) Trilayers." (Division Sponsor: B.W. Mangum)

July 1, 1992

Lori Torry Boock, Department of Chemical Engineering, University of Delaware, "Oxidation of Model Compounds in Supercritical Water: Experimental Kinetics and a Structure/Reactivity Model." (Division Sponsor: G.J. Rosasco)

July 8, 1992

A.R. Drews, Naval Research Laboratory, Washington, DC, "Room Temperature Screening for Superconductivity Using Optical Spectroscopy of $Y_1Ba_2Cu_3O_{7-\delta}$ ($0 < \delta < 1$) and $Nd_{2-x}Ce_xCuO_{4-y}$ (x near 0.15)." (Division Sponsor: B.W. Mangum)

July 9, 1992

Robert Zacher, Naval Research Laboratory, Washington, DC, " Superconducting Niobium Tunnel Junctions as X-Ray Detectors." (Division Sponsor: B.W. Mangum)

August 5, 1992

Carmela C. Amato, Rensselaer Polytechnic Institute, "The Gas Phase chemistry of an Aluminum Nitride Precursor, Trisdimethylanuminum Amide, $[(CH_3)_2AlNH_2]_3$, As Revealed by Molecular Beam Mass Spectrometry." (Division Sponsor: M.R. Zachariah)

August 17, 1992

Pratim Biswas, Department of Environmental Engineering, University of Cincinnati, "Particle Formation and Dynamics in High Temperature Systems: Applications in Waste Incineration and Materials Processing." (Division Sponsor: M.R. Zachariah)

11. Conferences/Workshops Sponsored/co-Sponsored**October 7-11, 1991**

Materials Processing Session, American Association for Aerosol Research (AAAR) 1991 Annual Meeting, Traverse City, MI (M.R. Zachariah)

October 8, 1991

Flow Meter Installation Effect Consortium Meeting, NIST-Gaithersburg, MD (G.E. Mattingly and T.T. Yeh)

October 21-25, 1991

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD (B.W. Mangum)

November 18, 1991

High Temperature Processing of Materials Session, American Institute of Chemical Engineers (AIChE) 1991 Annual Meeting, Los Angeles, CA (M.R. Zachariah)

March 9-13, 1992

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD (B.W. Mangum)

April 6-10, 1992

"Thin Film Sensors" and "Microsensors" Sessions at International Conference on Metallurgical Coatings and Thin Films, San Diego, CA (S. Semancik)

April 28 - May 1, 1992

Seventh International Symposium on Temperature, Its Measurement and Control in Science and Industry, Toronto, Canada (J.F. Schooley)

April 29, 1992

Workshop on Dynamic Temperature Measurement, Seventh International Symposium on Temperature, Its Measurement and Control in Science and Industry, Toronto, Canada (G.J. Rosasco)

May 1, 1992

Workshop on High Temperature Standard Platinum Resistance Thermometers, Seventh International Symposium on Temperature, Its Measurement and Control in Science and Industry, Toronto, Canada (B.W. Mangum)

July 6 - 7, 1992

Workshop on Federal Programs Involving Supercritical Water Oxidation, National Institute of Standards, Gaithersburg, MD (G.J. Rosasco)

September 29-30, 1992

SEMATECH/NIST Workshop on Chemistry of Chemical Vapor Deposition Processes in Semiconductor Manufacturing, National Institute of Standards and Technology, Gaithersburg, MD (J.R. Whetstone)

VII. Surface and Microanalysis Science Division (837)

Rance A. Velapoldi, Chief

A. Division Overview

The **Surface and Microanalysis Science Division** conducts research and development to (a) determine the chemistry and physics of surfaces, interfaces, particles, and materials, and their interactions with a broad spectrum of species including electrons, photons, ions, atoms, and molecules; (b) determine the chemical and isotopic composition and electronic structure of surfaces, particles, and materials at nanometer scales and above; (c) determine the energetics, kinetics, mechanisms, and effects of processes occurring on solid surfaces as well as within materials (or devices); (d) use chemometrics to study the total chemical measurement process as well as source apportionment in atmospheric chemistry; and (e) develop and certify Standard Reference Materials and Standard Reference Data. In these broad based efforts, emphasis is placed on performing fundamental and applied measurement research, providing data and standards (including software), and developing theories that are needed for accurately measuring chemical composition and dynamic processes that occur on surfaces, at interfaces, and in microstructures. This information is needed to understand the relationships between processing results, devices, or material properties and chemical composition in various technologies, such as chemical catalysis, advanced electronics, and materials science. This understanding provides the basis to develop new processes for bulk or specialty chemicals, advanced alloys and surface-modified, magnetic, and electronic materials.

Measurement Science. A significant part of our research in measurement science involves the development of new techniques and the application of state-of-the-art techniques to characterize chemical systems. We also apply the results of our research to areas of national scientific priorities for other government agencies, various industries, academia, and other areas in NIST.

Our efforts in collaboration with NIH on the NIST-NIH Nanometer Analysis Facility and on our 300 kV AEM have resulted in a breakthrough to achieve trace nanoanalysis, the determination of elemental concentrations at the ppm level with nanometer spatial resolution. We verified our initial measurements, performed preliminary quantitative measurements which yielded an ultimate limit of detection of 5-10 ppm atomic (equal to 5-10 atoms in a 10 nm x 10 nm x 100 nm sample volume containing 1 million total atoms), and applied the technique to specific problems including measuring nitrogen in diamond, determining the extent of homogeneity of lanthanum and rare earth elements in starting materials used to produce advanced magnetic materials (in collaboration with Nanophase Technologies Corp. and MSEL), and determining iron in nanometer-sized alumina particles, all applications that could not previously have been accomplished at these nm-scale resolutions. This information will be invaluable in determining trace contaminants, phase and chemical homogeneity in starting or end products, as well as assessing manufacturing procedures and their impact on chemical composition.

Particle sampling and analysis, including characterization of environmentally hazardous individual particles and populations of particles from various sources, constitute a significant effort within the Division. To determine the populations of particles in specific samples based on chemical composition, we are developing automated analytical techniques for ASEM and SIMS and using multivariate data analysis to evaluate the results. Efforts include studying the measurement process and determining the critical parameters and statistical limitations for achieving accurate analyses. Other areas in electron probe research include a new approach to micro-area x-ray fluorescence and applications such as the compositional mapping of industrially-produced high- T_c superconductors (with Biomagnetic Technologies), and numerous sample analyses for other Government Agencies. Our efforts in data accumulation (with 4-II Spectroscopy, Inc.), manipulation, and evaluation have continued by extending Desktop Spectrum Analyzer (DTSA), a comprehensive x-ray spectrum simulation and deconvolution calculation engine with an associated x-ray database. These efforts have focused on developing automated qualitative and quantitative analysis procedures that incorporate our expertise and which will eventually constitute a complete expert system for x-ray microanalysis. DTSA, offered for sale through the Office of Standard Reference Data during the past year, has sold almost 100 copies.

DTSA was used by Dr. Charles (Chuck) Fiori (its major developer), to increase the "practical" sensitivity of electron probe microanalysis by a factor of 5-10. He analyzed small crystals of a high- T_c superconductor non-destructively, demonstrating, for the first time, a practical measurement capability for electron probe measurements that approaches the limits of analysis for ideal situations in which there are no spectral interferences. Sadly, the unexpected death of Chuck Fiori has to be reported here. We have lost an innovative and productive scientist, a sensitive and caring colleague, and a good friend. We will certainly miss him - yet remember him throughout the years to come as we go about our tasks and lives which have been touched and enriched by so many of his contributions, actions, and witticisms.

The procedures developed and information obtained in these studies will be useful in several other microprobe techniques, including AEM and microbeam mass spectrometry (SIMS). Using this latter technique, we have investigated the mechanisms of the lithographic patterning of GaAs by STM (with MEL); characterized metal ion implants in InGaAs (with AT&T, NRL, George Mason Univ.); and imaged fluorine-tagged cocaine and PCP in human hair to assess the suitability of the artificially "doped" hair as an SRM (with Div. 835).

In other particle measurement areas, we have been collaborating with industry (Bubble Technology Industry, Inc.) to develop large-area bubble detectors for locating radioactive particle emitters in environmental radioactive analysis, as well as performing dosimetry studies and neutron beam mapping. In collaboration with the Army, we performed basic research aimed at leak testing of gas masks by studying the mass transport and flow of aerosols through orifices of known sizes. We have also worked with the National Fluid Power Association and the SRMP to initiate the production of a Particles-in-Oil SRM for use in calibrating instruments determining the size/mass distributions of particles in fluids.

Measurement and standards activities dominate our Congressionally mandated asbestos program. We have worked with more than 100 analytical electron microscope labs, the EPA, and the NIST NVLAP to attain quality analysis of airborne asbestos through a rigorous proficiency testing, standards, and methods research program. In the parallel program for analyzing bulk asbestos in building materials, PLM, quantitative XRD, and gravimetric methods have continued to be developed and used to characterize materials for the proficiency testing of more than 800 laboratories since the program's inception. We have essentially finished the research part of the program and instituted requirements for measuring semi-quantitative asbestos concentrations and optical parameters in proficiency testing. As a result, our plans for next year in the bulk asbestos program call for a significantly reduced quality assurance role.

Also in the environmental area, a major effort continues to make fundamental contributions to the areas of atmospheric measurements and standards. We provide leading-edge research and measurements in determining isotopic ratios of carbonaceous gases and volatile organic compounds to characterize the atmosphere on a local, regional, national, and global scale. Important studies this year include: a) the identification of ozone precursors (produced by exhausts of vehicles vs transpiration of vegetation); b) sources of potential organic carcinogens in the EPA's Integrated Air Cancer Project; and c) a comprehensive, integrated aerosol characterization study (species concentration, transport, sources, modeling, etc.) in the Los Angeles Basin. These efforts, made possible through our pioneering research in accelerator mass spectrometry micro-target preparation and chemistry for the determination of carbon isotopic ratios, will lead to elucidation of the effects of various sources on climate change. Installation of a new mass spectrometer this year to be used for determining carbon as well as other element isotopic ratios in gaseous species, and the acceptance of the responsibility for the maintenance and distribution of isotopic gas standards (formerly handled by the Chevron Oil Company and IAEA) strengthens our capability and commitment to provide measurement and standards help in the world-wide problem of global climate change. The NIST Primary Standard Reference Ozone Photometer, which has been updated, continues to be the benchmark standard for the global network [fourteen instruments in the U. S., Canada, Sweden, and Switzerland (currently being constructed)] on which worldwide ozone measurements are standardized.

The Chemometrics program has continued to focus on the total measurement process, and is linked closely with the above atmospheric efforts, providing an integrated effort for analysis, source apportionment, and modeling. Several other projects in chemometrics include DNA fingerprinting (with the FBI and Div. 831) which has defined interlaboratory error and set specifications for laboratory and data qualifications in round robin testing; the separation and quantification of vitamins (with Div. 835 and the NCI) in which variance of the individual steps were determined; the development of standard test data (with Div. 835) in pilot studies on liquid and gas chromatographies to establish algorithmic quality control; and automated particle analysis. Important fundamental work continues in chemometrics on multivariate data structure, quality, fundamental analytical limits (detection, identification, quantification), and accuracy -- closely integrated with and guided by the needs of national and international organizations.

These efforts are critical for common understanding, quality communications, and technology transfer in analytical and measurement science.

Measurement and Fabrication Science. An important challenge to various industrial sectors is understanding the mechanisms of thin-film growth with subsequent improvement of commercial manufacturing techniques. A technology with potential major financial impact involves magnetic thin films in applications such as magneto-resistive, non-volatile memory devices and short-wavelength optical storage media. As part of this effort, we have collaborations with IBM, Non-Volatile Electronics and the National Storage Industry Consortium. We have installed a unique, new facility in which we can, *in situ*, grow multilayer thin films by molecular-beam epitaxy and magnetron sputtering, characterize the chemical and structural properties of the films by an array of techniques, and determine the magnetic properties of the films. Simultaneously, we have used existing equipment and parts of the new facility to identify the thin-film growth modes of Co/Cu and Fe/Cu multilayer films which are strong candidates for a new generation of non-volatile computer memory chips. In related work, we have investigated theoretically how the magnetic coupling between two ferromagnetic films separated by a nonmagnetic spacer layer depends on the electronic structure of the spacer layer.

The reliable growth of commercial grade high- T_c films is a major obstacle for this important new class of materials that will only be overcome by an increased understanding of surface-related phenomena ranging from growth kinetics to the reactive interactions of the high- T_c film with various underlying substrates. Accordingly, in collaboration with the Univ. of Maryland's Center for Superconductivity Research and X-Sirius, Inc., we have grown thin films of high- T_c materials under controlled conditions in an ultra-high vacuum chamber equipped with several surface/interface diagnostics. We are correlating surface/interface information with macroscopic parameters such as T_c (critical temperature) and J_c (critical current density), as well as the final film microstructure and morphology with the effects of growth conditions. These measurements are providing information on how factors such as substrate preparation and morphology, and film deposition rate and temperature affect subsequent high T_c film characteristics.

To develop additional information for the electronics industry, we have used microprobe and measurement techniques such as XPS, AES, and the newly developed methods of grazing-angle photoemission spectroscopy and ultra-shallow depth profiling with SIMS to characterize surfaces and thin layers on GaAs devices after passivation. We were able to determine the presence of several different oxide layers that form by the diffusion of Ga and As through the passivating layer during various manufacturing steps, a result of critical importance in devising the best strategies for device passivation.

The development and use of diamond thin films as coatings for various high technology applications in the electronics, sensors, and machine tool industries is receiving increasing attention. We have used laser micro-Raman spectroscopy to evaluate the quality of industrial diamond thin films, first to establish an evaluative measurement procedure, and second, to

determine the suitability of the materials as potential diamond thin-film SRMs (in collaboration with Norton Industries and Raytheon, Inc.).

Surface Dynamics. In addition to the morphological and compositional characterization of materials and surfaces, we are investigating the dynamics of chemical processes that occur at well-characterized surfaces and interfaces. Using novel, state-of-the-art femtosecond spectroscopy along with nanosecond lasers and conventional surface sensitive probes, we are able to characterize surfaces and elucidate the underlying mechanisms of surface reactions induced by photons, ions, and thermal processes. The specific response of different chemical components as one ranges from deposition to removal of surface layers, provides critical information on the different energy transfer steps involved in the chemical process.

The ability to activate surface reactions without heating the underlying substrate is of great interest due to potential applications in areas ranging from electronic device fabrication to the synthesis of new catalysts. We have developed and used femtosecond laser techniques (with the Physics Laboratory) to investigate energy absorption and transfer between adsorbed surface species and the underlying substrate. This capability represents a significant advance in establishing mechanisms of non-thermal reactions. Understanding and controlling the coupling of optical radiation to the various species can provide the means for increasing selectivity in catalytic processes, tailoring surfaces for new semiconductor devices, and developing optically driven, low-temperature processing techniques to avoid material degradation.

As the experiments progress, we continually search for complementary models and simulations that provide a theoretical basis for these dynamic processes. Here we have developed models for the resonant inelastic scattering of wave packets that place localized quanta of energy into the reaction complex. We thus use short-lived, excited (hot) electrons and describe the dynamics following very diverse types of excitation, such as pulsed non-thermal laser excitation, resonant desorption of adsorbed atoms or molecules, and site-specific tunneling spectroscopy in scanning tunneling microscopy. The common focus in the applications is vibrational excitation which can lead to selective surface reactions through bond-breaking or desorption. We have also developed a new model for collisional de-excitation processes in ion-surface interactions to aid in the modeling of the ion-surface collision cascade in secondary-ion mass spectrometry and sputter-depth profiling, and to serve as a potential new means for surface chemical modification.

In the newly added capability of neutron scattering, we (in collaboration with Amoco, Univ. of Delaware, Univ. of California - Davis, and MSEL) have begun to characterize adsorbates bound to Ir clusters inside zeolites, and to establish the reorientation dynamics of cyclopropane, also inside zeolites. We plan to use the complementary measurement techniques of femtosecond spectroscopy and neutron scattering to provide dynamic and static studies of reactions and processes at internal surfaces, critical to so many industrial technologies using catalysis.

Standard Reference Data and Materials are needed to achieve accurate quantitative measurements. The initial X-Ray Photoelectron Spectroscopy Database, issued in 1989, has been modified to

become an easier-to-use Version 2 with additional evaluated data. We have also made a new series of calculations of electron inelastic mean free paths for a group of organic solids to aid industrial applications of quantitative surface and interface analyses using x-ray photoelectron spectroscopy (in collaboration with Div. 841) and extended the applicability of DTSA for quantitative SEM measurements. To aid in asbestos measurements, SRMs developed this year include a new SRM for tremolite, actinolite, and anthophyllite asbestos as well as significant efforts on a thin-film glass for use in AEM calibration.

Members of the Division received several honors this year. Dr. William Egelhoff was selected as a Fellow of the APS, Eric Steel received the Flemming Award from the Downtown DC JC's for "developing accurate measurements and standards to identify and quantify bulk and airborne asbestos", and Dr. Cedric Powell received the inaugural Riviere Prize for 1992 by the UK ESCA Users Group for 'work which has been judged outstanding in its continuing and lasting contribution to the application of electron spectroscopy'. In addition, we received one patent and submitted two patent applications. Strong interactions by the staff with our constituents and effective technology transfer are demonstrated by substantial technical outputs (see Section VII. C) and efforts to form new standards committees (e.g., guidance in the formation of Technical Committee 201 on Surface Chemical Analysis by the ISO and U.S. participation on this Committee), and participation on established committees. In addition, staff participated on evaluation and consulting panels for DoE, DoD, NSF, EPA, NRC, USGS, WHOI, and industrial groups. Finally, we have organized and participated in several international and national conferences. Information on individual technical contributions can be found in Section B.

**B. Selected Technical Reports
(Surface and Microanalysis Science Division)**

1. Tropospheric Ozone Precursors: Tracking Down the Sources of Volatile Organic Carbon

G.A. Klouda, J.E. Norris, G.C. Rhoderick (835), D.B. Klinedinst and L.A. Currie, R.K. Stevens (EPA), and C.W. Lewis (EPA)

It is well known that atmospheric non-methane volatile organic compounds (VOCs) play an important role in urban ozone formation during the summer. For effective strategies to control ozone, it is necessary to obtain a reliable assessment of the relative contributions of natural and anthropogenic VOCs to the airshed in question (Chameides *et al.*, J. Geophys. Res. 97, 6037 (1992)). To address the need for a direct measure of VOC source contributions (fossil [$^{14}\text{C}=0$] vs biogenic), we have performed gas phase separation chemistry and Accelerator Mass Spectrometry (AMS) ^{14}C dating, at the microgram level, to obtain exploratory ^{14}C measurements on the VOC fraction. The Gas Separation System developed at NIST allows for the simultaneous separation of $\geq\text{C}_5$ -VOCs, CO_2 and $\leq\text{C}_4$ -VOCs, CO and CH_4 through sequential cryogenic separation and selective oxidation techniques. Characterization of the system (blanks and recovery) is currently underway. Samples collected in Atlanta (1990) as part of the EPA Ozone Precursor Study, having total VOC concentrations from 427-904 ppbv-C, were processed to recover the $\geq\text{C}_5$ -VOC fractions for AMS ^{14}C measurements. Sample volumes recovered ranged from 44-66 μL ; for this sample size, our capabilities for measuring the ^{14}C abundance by AMS is at the 2% (1σ -Poisson) level.

2. Formation of a National DNA Fingerprinting Database

D.L. Duewer, L.A. Currie, D.J. Reeder (831), S.D. Leigh (CAML), H.K. Liu (CAML), F.S. Baechtel (FBI), and J. Mudd (FBI)

Restriction fragment length polymorphism (RFLP) analysis has become a routine forensic tool for DNA typing. While evidential use of RFLP is currently restricted to direct comparison of known and suspect tissue in the same assay, consistent determinations of RFLP, over time and among analysts, will greatly aid identification of individuals who commit multiple felonies. The Technical Working Group on DNA Analysis Methods (TWGDAM), with members from various local, state, and national forensic laboratories, recently completed a series of studies to determine the suitability of RFLP for such use.

We have completed the analysis of the TWGDAM studies and various supporting data and have determined that the standard deviation in the sizing of a given DNA fragment, over time and among laboratories, is a simple function of the fragment size: $\text{Std} = 10^{a + b (\text{Fragment size})}$, where a and b are empirically determined constants. This expected measurement uncertainty, expressed

as the % relative standard deviation, is less than 2% for DNA fragments of size 1000 - 8000 base pairs. In addition to demonstrating the stability of RFLP results, this result facilitates the robust comparison of DNA typing results.

We have also documented the magnitude of measurement variability in various steps of the RFLP process and identified several sources of bias among laboratories. This information is critical for making forensic RFLP methodology even more robust. We are currently exploring methods of determining the probable data quality of a given RFLP analysis and of documenting the stability of a given laboratory's results over time.

3. Regional and Global Sources of Greenhouse Gases: the Critical Role of Isotopes

J.M. Conny, L.A. Currie, and A.M. Thompson (NASA)

In addition to the major species carbon dioxide, several other trace tropospheric gases, including methane, are responsible for climatic change due to their infrared trapping properties. To control anthropogenic input of these gases, regional and global production estimates from both natural and anthropogenic sources are required. Accurate emission estimates for CH₄ are particularly difficult to obtain because of the many natural and anthropogenic source types (e.g., wetlands, ruminant emissions, rice paddies) and widely varying flux measurements for some sources. Relying upon different rates of isotope fractionation that are independent of flux, carbon and hydrogen isotopic measurements (¹³C, ¹⁴C, ²H, ³H) provide unique signatures for different sources. Agreement between CH₄ source isotopic composition and the isotopic composition in ambient air provides a critical constraint to models that accurately and precisely estimate tropospheric CH₄ emissions with sufficient spatial and temporal resolution on global and regional scales.

To meet modeling needs in isotopic accuracy, precision and resolution, we are compiling and evaluating a database of existing source and ambient CH₄ isotopic signatures along with those of its oxidation product, CO. New methodologies based on source/receptor modeling are being developed for determining where to sample most cost-effectively. Measurements based on these sampling design strategies will help determine uncertainty requirements for matching source with ambient CH₄ and CO isotopic composition, evaluate uncertainties in the extant database, and identify sources that are, at present, inadequately characterized.

Initial modeling work focuses on the isotopic composition of source and ambient CH₄ in Brazil during the early dry season (July-August). From meteorological trajectories, upper boundary layer air (altitude ~1.3 km) originating along 50°W, between 5 °S and 20 °S, changes direction sharply near 20 °S. Air masses to the north move easterly, and ambient samples likely reveal the ¹³CH₄ isotopic composition of burning savanna grass emissions (δ¹³C=-33 to -10‰) or Amazon wetland emissions (δ¹³C=-73 to -42‰). Air masses south of 20 °S move westerly and might

reveal the $^{13}\text{CH}_4$ composition of burning sugar cane ($\delta^{13}\text{C} = -19$ to -10), an agricultural practice known to occur widely in the Minas Gerais and Goias provinces of Brazil.

4. Atmospheric Standards for Ozone, Methane, and Carbon Oxides

R.M. Verkouteren, G.A. Klouda, and J.E. Norris

Accurate chemical and isotopic measurements of atmospheric trace gas distributions are extremely important for understanding their influences on local air quality and regional/global climate, and for the identification of their sources. As worldwide awareness and monitoring of atmospheric gases increases, so does the need for a wide range of standard analytical methods and relevant reference materials.

Our primary ozone photometer is used as an instrumental reference standard for 13 replicate units manufactured at NIST and operated globally by the EPA, U.S. industry, and international organizations. More than 10 calibrations were performed for industry and EPA; they show that the accuracies of these instruments range from 2 -20 ppbv over the range 0 - 1000 ppbv O_3 . We anticipate several new orders for these instruments as the global ozone monitoring network grows.

We are developing the first multi-isotopic (^{13}C , ^{14}C , ^{18}O) gas reference materials using pure carbon dioxide, carbon monoxide, methane, and blends of these gases. A parallel-process gas homogenization manifold was designed for the precise preparation of over 1000 units of gas, isotopically (and chemically) identical to within 10 parts-per-million. A high-precision gas isotope ratio mass spectrometer (Finnigan MAT 252) was recently purchased to enable precise measurements of ^{13}C (< 10 ppm "external" precision) and ^{18}O (< 30 ppm); measurements of ^{14}C (< 4000 ppm) are performed by Accelerator Mass Spectrometry at a collaborating laboratory. The availability and use of these gases will allow more accurate isotopic standardizations of instrumental systems worldwide by avoiding biases introduced during chemical separations and conversions of less appropriate reference materials; the range of available isotopic gas compositions will closely resemble the biogenic and anthropogenic sources of these trace gases.

5. Total Quality Measurement: An International Perspective

L.A. Currie and G. Jones (Woods Hole Oceanographic Institute)

Total Quality Management (TQM) has evolved as the highest level of a process that began in the early 20th Century as Quality by Inspection. Quality Management has acquired such international importance that it has become codified under an International Standard (ISO-9000) of the International Organization for Standardization (ISO) to provide guidelines for the assurance of quality of products and services on a global scale. Key attributes of TQM are the definition

and quantification of quality, attention to the *entire* quality system, and involvement of all organizational levels in the implementation of a quality strategy. Total Quality Measurement may be viewed as the metrological component of TQM. As such, it requires: an appropriate definition of measurement quality, attention to the *entire* measurement process, and a broad multidisciplinary approach for the assessment and achievement of measurement quality.

Major efforts are currently being made to develop internationally acceptable definitions of measurement quality and metrological performance characteristics. Through our work with IUPAC, for example, we have taken the lead in establishing international nomenclature for detection decisions and detection limits for chemical measurement processes. Acceptance of the IUPAC nomenclature by a larger international (metrological and health) community appears imminent as a result of liaison during 1992 with ISO and WHO (FAO Committee on Methods of Analysis and Sampling). The latter committee bears the responsibility for certifying measurement methods for the detection of toxic elements in foods.

During FY92 we had a special opportunity to apply the total quality measurement paradigm to a large, global environmental (climate) program concerned with the transport of CO₂, heat and pollutants by the world's oceans: the World Ocean Circulation Experiment. The experiment demands ¹⁴C measurements of unprecedented throughput (4000 per year) and accuracy (0.5%). Work at the Woods Hole Oceanographic Institution (WHOI) accelerator mass spectrometry laboratory has shown remarkable progress in extending the state of the measurement art to meet these goals, through exhaustive multidisciplinary (chemical, physical, statistical) analysis of every step of the measurement process. Noteworthy in this effort has been the interplay between exploratory data analysis and scientific insight leading to fundamental gains in process quality.

6. Trace Nanoanalysis: Measuring Trace Concentrations at Nanometer Scale Spatial Resolution

D.E. Newbury, E.B. Steel, and R. Leapman (NIH)

Trace nanoanalysis, the detection of dilute trace constituents from sample volumes with nanometer dimensions, was first reported in FY91 as a result of a collaboration between NIST and NIH scientists working at the NIST-NIH Nanometer Analysis Facility. Measurements of dilute trace constituents, at the level of parts per million and approaching single atom sensitivity, were made from areas of 10 x 10 nm by means of parallel detection electron energy loss spectrometry (PEELS). These measurements are made in the field emission scanning transmission electron microscope (FE-STEM), a form of analytical electron microscope (AEM). PEELS measures the characteristic energy losses suffered by energetic beam electrons (100 keV or greater) that pass through a thin (100 nm or less) specimen and inelastically scatter with bound electrons in the atomic shells. Extending PEELS measurements to trace sensitivity depends on the occurrence of "white lines," which are narrow spectral features having a high peak-to-background, that arise from solid state electron resonance effects. The electron loss spectra of

many elements show these features, particularly when the elements are combined in compounds such as oxides. These narrow features are selected against the generally high spectral background by processing with the "second difference" algorithm that utilizes three spectra obtained with energy offsets. By offsetting the spectra on the array of parallel detectors, the true spectral background as well as the major instrumental artifacts are eliminated from the calculated second difference spectrum.

The original work that demonstrated the possibility of trace nanoanalysis was performed on NIST SRM 610 trace element glass. Transition metal, alkaline earth, and rare earth elements were successfully detected at concentrations from 50 - 200 parts per million atomic. Subsequent measurements on other materials have demonstrated detection of trace levels of low atomic number elements (nitrogen and oxygen) and inert gas elements (argon in SRM 2063a and diamond), and to a variety of crystalline materials. The original measurements at 100 keV on the FE-STEM have been successfully repeated at 300 keV on a conventional source AEM at NIST; increased beam energy provides greater sample penetration and the possibility of using thicker specimens. We have also demonstrated the possibility of making quantitative concentration measurements at trace levels by means of a simple sensitivity factor determined on major constituents in a stoichiometric compound (Ba in SRM 610 vs Ba in BaCO₃). This sensitivity work also permitted an estimate of the limit of detection, which was approximately 5 -10 parts per million atomic. Trace element detection in the presence of a potentially severe spectral interference from a major constituent was demonstrated for Sc (240 ppma) in Ca (0.044 atom fraction) with a ratio of 1:200. Trace nanoanalysis has been applied to practical problem solving in materials science: e.g., by measuring the concentration and spatial distribution of nitrogen in diamond; lanthanum and other rare earths in nanoscale yttrium oxide for magnetic applications; and iron in nanoscale aluminum oxide. A possible environmental application to the characterization of trace elements in volcanic ash has also been explored.

7. Automated Electron Probe Analysis of Particulate Populations: Measurement Precision Limitations

J.A. Small and M.A. Calderone

Scientists have performed the analysis of large numbers of particles by automated scanning electron microscopy/electron probe microanalysis (ASEM) in conjunction with multivariate analysis algorithms to classify particles into different groups based on size, shape, and elemental composition. These groups (clusters) and the number of particles belonging to each are often used to estimate macroscopic characteristics associated with the particle population, such as the development of source apportionment for a sampled aerosol.

The precision associated with the x-ray analysis of the individual particles directly affects the size or spread of the different particle groupings that are based on elemental compositions. In the case of low measurement precision, different particle groupings may overlap, making it

impossible to group particles correctly and to assess the percent of the sample population accounted for by a specific group. Thus poor precision significantly limits the information that can be obtained from a sample. One factor that affects measurement precision in ASEM analysis is the relatively short x-ray counting times, typically between 0.1-30 s, used for the accumulation of x-ray spectra from the individual particles. In comparison, the counting time used in conventional single point electron probe analysis is on the order of 100 - 1000 seconds per measurement.

We have conducted a series of theoretical calculations and experimental measurements on analytical glasses to relate measurement precision to analysis conditions. This relationship establishes our ability to identify particle groupings correctly based on elemental compositions at the trace, minor, and major concentration levels. For this work, a series of six glasses containing varying amounts of uranium (0.8 wt% to 17 wt%) in a silicon (14%) -oxygen (27%) - lead matrix (42-59%) were synthesized and analyzed as both bulk and particle samples. The high lead constituent provided a nearby peak to interfere with the peaks of the uranium constituent. In addition to the uranium, each glass was doped with a trace level, approximately 1% by weight, of a metal oxide with a well separated x-ray peak to serve as a tracer for that glass. The tracer was used to identify each specific glass composition even when the measurement statistics did not permit recognition based upon the Pb/U ratio. This tracer served the further function of providing an estimate for the limit of detection of a trace constituent in the absence of peak interferences.

The results from the theoretical calculations of the bulk glass x-ray spectra, simulated with the NIST DeskTop Spectrum Analyzer calculation engine, are in good agreement with experimental bulk measurements. The results indicate that at the short counting times, less than 1s, measurement precision is so poor that it is impossible to identify the individual glasses. Substantial overlap exists between the different compositional groups even at an analysis time of 15s. In addition, the detection limits for the short analysis times, less than 0.5s, indicated that in almost 50% of the analyses the tracer element was not detected, and in about 10% of the analyses for uranium as a major constituent at 17 wt%, the uranium was missed. Results from the experimental measurements on particles indicate that the measurement precision for a given analysis time is considerably worse than the corresponding bulk analysis. As a result, particle analyses may need to be on the order of several minutes to obtain useful results.

8. Detectability of Objects in Noisy Electronic Images by Computer Image Simulation

D.S. Bright, D.E. Newbury, and E.B. Steel

A general problem in microscopy is the recognition of low contrast features in noisy images. This situation is often encountered in scanning electron microscopy, where the threshold of visibility is one of the most important, yet least appreciated concepts. "Detectability" refers to whether a feature can be recognized against a general background of other objects when a search

must be conducted. To improve detectability, the relative noise level is often reduced at the cost of increased image collection time, beam current, or detector efficiency. By relating the improvement to the cost, we can use data collection time to best advantage. Many studies have been done on the visibility of various noise-free patterns as a function of absolute brightness and contrast. Our study of objects presented on a CRT measures the discriminating ability of the eye in the presence of random noise for ambient lighting levels. Albert Rose measured the visibility of simple objects in noisy images in the 1940's in the process of investigating image quality for the television industry. We have adapted Rose's work to the study of digital images obtained by electron microscopy and have expanded on his results.

We constructed test images with objects presented on a uniform background, and then added Poisson noise to both the objects and the background. The objects were simple geometric shapes such as squares, lines, disks and hexagons, or copies of actual metallic grains taken from micrographs. The observers had to identify the objects by marking them to indicate the shape and outline. Most objects were barely discernible, and appeared amongst a varying number of other objects. The observers were shown the types of objects to expect, the way they were to be identified, and the expected size range for the objects. The number, type, location, contrast and orientation of the objects were not known to the observers ahead of time.

We have found that object detectability or visibility depends only on K , the ratio of signal-to-noise integrated over the object. This relationship held over a wide range of parameters including object contrast, noise levels, object area, object shape, and age or experience of the volunteers. The result concerning object shape means that if the objects have equal contrast, detectability is similar for disks and straight lines of equal *area* and not equal linear dimension or equal angle subtended at the eye. This result was unexpected because it indicates a remarkable capability of the human visual system to adjust its "data collection" to the shape of the object. There is a transitional area above which detectability is not improved. This area corresponds to a disk subtending about two degrees in the field of view, which is approximately the size of the fovea. For object detection only, K does not strongly depend on object shape, on the distinctness of the edges, or on whether the objects are brighter or darker than the background. The integrated signal-to-noise ratio for marginally detected objects is on the order of eight to ten. Other factors such as image resolution and shape discrimination were also studied.

9. DeskTop Spectrum Analyzer (DTSA): Comprehensive X-Ray Analysis

C.E. Fiori (deceased), R.L. Myklebust, and C. Swyt (NIH)

DeskTop Spectrum Analyzer, a comprehensive program for electron excited x-ray spectrometry, was offered for public sale by the NIST Office of Standard Reference Data early in FY92. As described in the FY91 highlights, DTSA emulates the specimen properties, electron excitation conditions, and the experimental environment to generate spectra *ab initio* that fully represent

the relevant physics, chemistry, and statistics of a specimen under electron bombardment. The program has been developed for the Apple MacIntosh II series of computers and enables the analyst to generate, display, interpret, deconvolve, and quantify x-ray spectral data from electron column instruments, including scanning electron microscopes, electron probe microanalyzers, and analytical electron microscopes. With an appropriate Nu-buss card installed in the computer, the program can also acquire x-ray spectra directly.

One important mode of operation of DTSA is to estimate the limit of detection on a sound statistical basis for a particular analytical situation. In this mode, the DTSA is used to generate an x-ray spectrum from first principles that will be comparable in all of the germane physical and statistical properties to an actual spectrum from a real specimen. From the generated spectrum the analyst can then deduce accurate estimates of variance about mean compositional values. The analyst can also accurately estimate the minimum detectable limit (MDL) of any analyzable stable element in any stable matrix, without the need to produce a set of calibration standards. Furthermore, the experimental parameters can be adjusted to determine the optimum set that will produce the lowest MDL. All of this can be done relatively rapidly before making a single measurement on the electron microprobe, thus freeing time for more productive use of this expensive equipment.

Significant enhancements to DTSA have been developed since the shipment of version 1.0, including the incorporation of automated qualitative analysis, automated window selection for peak deconvolution for quantitative analysis, sensitivity factor analysis for analytical electron microscopy, wavelength dispersive x-ray spectrometry to augment the energy dispersive spectrometry emphasized in the first version, and numerous features to improve the manipulation, labelling, and display of spectra. Further developments are anticipated as DTSA evolves into an expert system for x-ray microanalysis.

We have applied for a patent for the DTSA program and the application is currently in review at the U. S. Patent Office. This submission apparently represents the first such application on software made in the Department of Commerce.

10. Trace Analysis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Single Crystals by Electron Probe X-ray Microanalysis

C.E. Fiori (deceased)

Non-destructive trace analyses was performed by electron probe x-ray microanalysis (EPMA) with wavelength-dispersive x-ray spectrometry (WDS) on materials produced in the high T_c superconductivity research program in the Materials Science and Engineering Laboratory (Debbie Kaiser). The materials research was directed toward the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals with controlled doping of various elements, e.g., silver, silicon, manganese, and calcium, to replace selectively matrix elements and explore the chemical effect on superconducting

properties. Although the single crystals grown by MSEL are some of the largest ever produced, they typically have dimensions ranging from only 50 to 300 micrometers and a mass of a few micrograms, making them a difficult subject for a conventional bulk trace analysis method. The difficulty in synthesizing crystals makes it imperative that they be analyzed non-destructively so that they can be retained for subsequent study.

Microanalysis by WDS in the electron probe microanalyzer is non-destructive and can reach limits of detection in the range 10 -100 ppm. Such low limits of detection can only be achieved in ideal situations where there are no spectral interferences from high intensity peaks of matrix constituents. Because of the high spectral resolution, most WDS analyses at the major and minor constituent level are normally regarded as interference-free. The situation is much more complicated when measurements are to be performed at the trace level because of the extensive family of characteristic x-ray peaks that arise from high atomic number elements, e.g., barium, the presence of satellite lines associated with high intensity peaks, and the occurrence of spectral features that result from the operation of the integer multiplicity factor in Bragg's law (high order lines). To accommodate this situation, DTSA was substantially expanded to include wavelength dispersive spectrometry. The DTSA x-ray database is comprehensive and includes the complete x-ray families as well as satellite lines. A mathematical algorithm describing the Lorentzian shape of the WDS peak was incorporated into the peak deconvolution scheme based upon the sequential simplex approach. This deconvolution permitted accurate subtraction of the influence of nearby high intensity peaks, an important consideration because of the wide extent of the shoulders of Lorentzian peaks. Accurate peak intensity extraction led to high confidence measurements of doping levels in the superconductor crystals ranging from 1000 to 6000 parts per million by weight. This study was the impetus for an important enhancement in the capabilities and analytical performance of DTSA.

11. Certification of SRMs for Asbestos

S. Turner, E.B. Steel, J.M. Phelps, E.S. Windsor, J.R. Verkouteren, and S.S. Doorn

The detection and analysis of asbestos in building materials, water and air are of interest to a wide variety of commercial, government and academic laboratories for the study of health-related effects, the determination of need for abatement procedures, and for the determination of the cleanliness of air after abatement of asbestos from a building. Standards are needed to calibrate the analysts, equipment, and laboratory procedures, and to detect the presence (or development) of biases in the identification and concentration of asbestos reported by the laboratories.

SRM 1867: Bulk Asbestos-Uncommon (Anthophyllite, Actinolite, and Tremolite): Hundreds of laboratories in the U. S. use polarized light microscopy (PLM) to analyze building materials for the presence of asbestos. The laboratories need standards of the six regulated asbestos minerals to determine their proficiency at identification using PLM. The six regulated asbestos types have

been issued as two SRMs; SRM 1866-Common Commercial Asbestos and SRM 1867, which has just been completed, contains the three remaining uncommon asbestos types. These latter asbestos materials, anthophyllite, actinolite, and tremolite, present more technical difficulties for the laboratories because they are encountered infrequently and they are more difficult to analyze. They display biaxial optical properties instead of the pseudo-uniaxial optical properties observed for the three commercially common types of asbestos, which requires the analyst to select for measurement only those fibers that display appropriate orientations. The certified properties given for the three asbestos types in SRM 1867 include refractive index and dispersion for α , β , and γ , extinction angle, birefringence, color, and sign of elongation; these values were determined using spindle stage techniques and the double variation method of refractive index measurement. We also provide information values for the composition of each asbestos type, determined by electron probe microanalysis. The three asbestos samples in SRM 1867 will be useful to the laboratories as training materials for the measurement of refractive indices on fibers exhibiting orientation effects, and for the measurement of all the optical properties necessary for a positive identification of the three uncommon types of asbestos.

A byproduct of this work is the establishment of the capability to make refractive index measurements. We have inherited equipment and developed the expertise as other groups at NIST decided to discontinue their efforts. We have a number of techniques available for very precise and accurate measurements of the refractive index of liquids, glasses, and anisotropic particles, and the variation of refractive index with respect to wavelength and temperature.

SRM 1876b: Chrysotile Asbestos for Transmission Electron Microscopy: In measuring asbestos in air (or liquid), the "matrix" is sampled by drawing it through filters leaving particles on the filter surface or interior. The concentration of asbestos on filters is then determined by labor-intensive application of transmission electron microscopy (TEM).

A new SRM for the TEM procedure of asbestos analysis on filters has been produced. The standard was developed by depositing chrysotile onto an array of mixed-cellulose-ester filters using an aerosol generator. The loading and the homogeneity of the loading were extensively characterized by NIST and numerous laboratories, yielding two major results. First, it was possible to evaluate in depth the asbestos analysis method developed by the Environmental Protection Agency. Problems were found in the counting rules (method for determining the amount of asbestos in a particle). A modified set of rules has been developed to allow for consistent analyses; these rules are presently being considered as replacement for the EPA rules. Second, the loading was found to have a Poisson distribution and a certified value for the filter loading could be determined. Laboratories can use the SRM for training new analysts and for quality assurance of results from more experienced analysts.

12. Ultra-Shallow Depth Profiling by Secondary Ion Mass Spectrometry to Characterize Passivated GaAs

J.A. Bennett and J. Dagata (MEL)

The measurement of ultra-shallow distribution profiles or abrupt transitions in material composition is essential in materials research, particularly in the development of future semiconductor devices. Current analytical methods are severely challenged by the next generation of processed materials. Our goal is to apply ultra-shallow depth profiling to technologically relevant materials, (e.g., compound semiconductors, corrosion-resistant metals), and demonstrate the utility of the technique. An excellent example of the utility of ultra-shallow depth profiling is demonstrated in the study of GaAs surface passivation.

The ability to reduce the reactivity, or passivate, semiconductor surfaces plays an important role in the successful processing and manufacture of semiconductor devices. Unfortunately, the compound semiconductors (GaAs, InP, AlGaAs, etc.) present a chemical and electrical environment that is difficult to control, particularly with regard to surface state defect densities. Some success in the passivation of GaAs has been achieved using sulfur-based chemical treatments. Our investigations involve the use of $P_2S_5/(NH_4)_2S$ etch solutions and UV/ozone oxidation treatments to passivate the GaAs surface.

The key to successful passivation is to keep the passivating layer thin and uniform. We have modified the software used to control our time-of-flight secondary ion mass spectrometer (TOF-SIMS) to operate in the depth profile mode to monitor the elemental and molecular ion distributions in the thin passivating layer. The parallel detection of secondary ions allows for the efficient use of sputtered material, making it possible to collect meaningful depth profiles from extremely thin layers (less than 20 nm thick).

From the TOF-SIMS data we have established that etching GaAs with the $P_2S_5/(NH_4)_2S$ solution leaves the surface covered with a well-ordered, monolayer thick oxide consisting of predominately arsenic oxides. Hydrocarbon contamination is less than a monolayer thick. The ultra-shallow depth profiles also indicate that traces of S remain in the passivating oxide layer as a result of the chemical etch. The electrical properties of the passivated GaAs are improved (i.e., lowering the surface state defect density) by exposing the sample to a UV/ozone oxidation treatment. Ultra-shallow depth profiling was used to follow the changes occurring in the GaAs as a function of UV/ozone treatment times. The arsenic-oxide-rich surface changed very little during the growth of the sub-surface oxide, growing only slightly thicker. A sub-surface oxide, rich in gallium-oxides, appeared at exposure times greater than 15 minutes and grew to a thickness of about three nm after 45 minutes. A portion of the S originally present as a contaminant in the top arsenic-oxide-rich layer was redistributed into the gallium-oxide-rich layer during the UV/ozone oxidation.

The ability to monitor the changes in elemental and molecular ions in layers less than 20 nm thick has provided valuable insight into the passivation mechanism and certainly will be useful in improving the passivation process.

13. Transition Metal Ion Implants in InGaAs Measured by Secondary Ion Mass Spectrometry

D.S. Simons, S. Gulwadi (George Mason Univ.), and R. Mulpuri (George Mason Univ.)

In_{0.53}Ga_{0.47}As (hereafter InGaAs), lattice-matched to an InP substrate, is a potentially important material for optoelectronics and microwave devices. It is important for some of these applications to create semi-insulating (SI) layers in the material. Some possible uses would be in photodetectors, heterojunction lasers, and device isolation regions in monolithic integrated circuits. As grown, InGaAs is usually n-type due to residual impurities such as Si and S. One way to achieve SI layers is to dope InGaAs with transition metal ions that introduce deep acceptor levels in GaAs and InP. Fe has been added to InGaAs during growth for this purpose, but the Fe concentration and the resistivity of the material are difficult to control. An attractive alternative method for introduction of transition metals is ion implantation which offers good control over the dopant concentration and depth distribution. However, it does require a subsequent annealing step to heal the implantation-induced lattice damage which can give rise to a redistribution of the dopant, adversely affecting the device performance.

A study of the redistribution of transition metal ions implanted into InGaAs was undertaken using secondary ion mass spectrometry (SIMS) to profile the implanted species before and after various annealing treatments. The transition metals implanted were Ti, V, Cr, Fe, and Co at an implant energy of 380 keV and doses ranging from $3\text{--}5 \times 10^{13}$ atoms/cm². In some cases the target was held at room temperature, and in other cases at 200 °C. Rapid thermal annealing was done at temperatures from 700 °C to 900 °C for 5 s. The SIMS depth profiles were made with an O₂⁺ primary ion beam at an impact energy of 8 keV. Positive secondary ions of M⁺ (M=transition metal) and As⁺ were monitored. The concentration scales were determined from a relative sensitivity factor of M to As that was derived by normalizing the depth integral of the as-implanted sample to the stated implantation dose. The depth scale was established for each profile by measuring the crater depth with a stylus profilometer and assuming a constant sputter rate in the InGaAs.

A variety of redistributional effects were detected for the different transition metal implants. The profiles of Cr and V implanted at room temperature have the expected Gaussian shape over several decades of concentration before annealing. General features of the profiles after annealing are the outdiffusion of the implanted species to the surface and the appearance of a multiple peak structure. Cr is much more strongly redistributed than V under similar annealing conditions. Results for Fe were similar to those for Cr. The multiple peaks can be attributed

to several distinct processes: the gettering of implanted atoms by residual implant damage, the formation of precipitates involving the implanted species and As atoms, and the condensation of point defects into dislocation loops in the implant tail.

SIMS depth profiles for Co and Ti implanted into InGaAs at 200 °C show that outdiffusion of the implanted species to the surface still takes place, even for the as-implanted Co. However, the multiple peak structure of the room temperature implants no longer occurs. This is attributable to the easier removal of lattice damage by annealing for the elevated-temperature implants, as confirmed by RBS measurements. The Ti implant showed the smallest redistribution after annealing of all of the transition metals. This implant was done into p-type InGaAs because of the donor levels (n-type) that were expected for Ti. For the 850 °C anneal, the resistivity was almost at the intrinsic limit and there was minimal redistribution of the Ti. This suggests that Ti implantation into p-type InGaAs will be an attractive method for obtaining high resistance layers.

14. Imaging the Distribution of Drugs of Abuse (Cocaine, PCP) in Human Hair by Secondary Ion Mass Spectrometry

J.G. Gillen and M. Welch (835)

There is interest in the development of analytical techniques for the identification of drugs of abuse in human hair. The analysis of hair is attractive because the method is non-invasive and compounds are stable in hair for extended periods of time, thus giving a clearer indication of habitual drug use. However, there are still a number of fundamental questions that must be resolved. The precision and accuracy of new methods for hair analysis are characterized by the use of reference materials that are often prepared by soaking blank hair samples in solutions containing the compounds of interest. There is some evidence that differences in hair type may result in variations in drug incorporation and therefore may not reflect "standard" behavior for hair. There is also a question about the effect of various treatments that could potentially be used by drug users in an effort to avoid detection. It has also been suggested that environmental contamination of hair samples could lead to false positive results. In this preliminary study, we have evaluated the feasibility of using SIMS for imaging the distribution of labeled compounds in human hair. Our initial experiments involved soaking various hair samples for several days in a saturated solution of either fluorinated cocaine or brominated PCP (courtesy of D. Kidwell, Naval Research Laboratory). Short sections of hair (~ 0.5 cm in length) were mounted by dropping them onto conductive silver paint smears on metal substrates and in epoxy. These samples were then microtomed to produce cross-sections ~1-4 μm in thickness. The microtomed samples were analyzed in a secondary ion microscope/microprobe under Cs^+ bombardment while monitoring negative secondary ions. In all cases, either the F^- or Br^- secondary ion signals were used as markers to localize the position of the molecule. In cross-section, the compounds were found mainly in the periphery of the hair, penetrating 10-20 micrometers below the surface. This non-uniform distribution would not be desirable in a standard hair material. Several types

of hair were examined (different natural colors, dyed and permed) and very similar distributions were found. Surface imaging along a strand of hair indicated that the compounds were uniformly distributed. We also discovered that, in some cases, sufficient signal could be obtained from the parent molecular ion of cocaine to generate an image. SIMS may be useful for evaluating surface contamination effects and raises the possibility of localization studies without the need for using labelled compounds. Thus, from these experiments, SIMS could be a valuable tool for studying both the mechanism of drug incorporation in human hair and the influence of various external treatments on the re-distribution of drugs in the hair matrix.

15. A Novel Bubble Detector for Localizing Point-Source Radioactive Emitters

C.J. Zeissler

Bubble detectors, normally used for bulk gamma and neutron radioactivity dosimetry, have been developed for performing the localization of point-source radioactive emitters, in a collaborative effort with industry. The principle behind radiation detection with bubble detectors is similar to the classic cloud chamber used in ionizing radiation track imaging, although in the reverse mode. Like the cloud chamber, which uses a phase change (gas to liquid) to image the path of ionizing particles through a gas, the bubble detector uses a phase change (liquid to gas) to detect radiation. This technology, about one decade old, is offered commercially for immediate-read gross neutron dosimetry. This work however, involves new developments aimed at radioactivity imaging.

In the bubble detector design developed in this work, small liquid drops (no larger than a few hundred micrometers in diameter) of a freon mixture are dispersed in an aqueous gel. By manipulating pressure or temperature (depending on the design) during manufacture, storage or use, the detector may be activated by superheating the liquid droplets. The passage of high energy photons, beta particles or alpha particles through the metastable superheated liquid bubble will destabilize it to cause a phase change to the gas state. This change is accompanied by both an audible pop and the formation of a gas bubble larger than the original liquid droplet, held in place in the gel medium. The gas bubble is more visible than a liquid droplet because of an increase in size and an increase in the difference in refractive indices between the medium and the bubble. With a suitable bubble diameter and population density in the gel, it is possible to create an image in the gel corresponding to the amount of radioactivity emitted by a sample held in close proximity to the detector. The detector is reusable by in-situ recompression of the formed gas bubbles back to a liquid state. Two basic designs have been made and tested. In one, the detector is kept under pressure to maintain stability until use, and in the other, the detector is stable until heated in an oven or on a hot plate. Then the sample is applied to the surface of the detector which is protected by a plastic film, the exposure takes place, and the bubbles formed are both audible and visible. Compositions and adjustments of gel constituents allow for long term storage, response linearity, sensitivity selectability, and neutron detection. The bubble detector imagers are currently capable of a spatial resolution of approximately 5 mm

for ^{137}Cs and ^{75}Se point sources in the nano- to micro-Gray range. Major advantages over other position-sensitive radiation detector technologies (e.g., nuclear films or thermal luminescence dosimetry (TLDs)) include large active surface area (20 cm diameter), the ability to image less than 500 dpm gamma ^{137}Cs point-sources as well as neutrons, alpha and beta particles, approximate human tissue equivalence for dosimetric applications, live-time readout, response selectivity, reusability and ease of use. Bubble detectors for gross measurements are being explored by the Health Physics community because the absorption of ionizing radiation by bubble detectors is more analogous to the absorption of living tissue than the absorption and related physics involved in TLD and similar detectors. Response repeatability is better than 10% when performed on a daily basis for over a year for commercial bubble detectors designed for bulk neutron dosimetry. At this time, the detectors modified for imaging experience degradation with use, although the success of the bulk measurement designs make repeatability promising for future bubble imagers. Potential applications include environmental radioactivity analysis, dosimetric studies, beam mapping, and possibly field applications where electronic support would be lacking.

16. Micro-Orifices as Controlled Leaks for Respirable Mask Testing

R.A. Fletcher, E.S. Etz, R.M. Verkouteren, and S.A. Wight

Leak test systems often use submicrometer airborne particles (aerosols) as test agents. These test aerosols challenge both the filter components and the seal of the mask to the user's face. Direct, empirical verification of the particle detector response to low concentrations of particles produced by the test system is difficult and not always possible. In quantitative mask testing, the calibrant is usually assumed to have a linear response with respect to the particle concentration. We are studying aerosol and air transport through micro-orifices with the intention of using such devices to create controlled leaks characterized for the precision of the flow rate of air and particles. One major aspect of the study is to determine if particle size distributions are preserved during aerosol transport through the orifice. This is important because the aerosol sensor is an optical light scattering device that has a particle size dependence with respect to its electrical response.

Measurements have been made employing single orifices in the size range of 10 to 50 μm diameter. The transport is produced by a small pressure drop across the orifice ranging from 500 to 5000 Pa. Under laboratory conditions, the flow rate is on the order of 0.1 to 5 mL/min which corresponds to Reynolds number flow through the orifice in the range of 1 to 100. Leak rates based on air measurements are estimated to be from 0.07 to 4 $\mu\text{mol/s}$. Particle-free air is produced by triple filtering the pressurized laboratory air source. Flow rate dependence on pressure drop was determined for particle-free air flow and for a polydisperse oleic acid and alpha olefin aerosol with number mean size of 0.3 μm . Aerosol was generated using a Laskin type droplet generator coupled to three conditioning reservoirs that serve to stabilize the particle size distribution. Particle size distribution was determined using a high volume cascade impactor and flow rates were measured by two methods. The particle concentration of aerosol passing

through the orifices was measured using a continuous flow condensation nuclei counter. Results indicate that the flowrates of particle-free and particle-laden air are approximately the same. The air flowrate can be compared to the particle number count (particle concentration) that is transported through the orifices. In this case, results indicate that flowrates measured using either a gas flow meter or particle counter have similar transport for the case of particles through large orifices, but for the smaller orifices (hole diameter $< 30\text{ }\mu\text{m}$) the particle count indicates reduced transport relative to the pure air measurements. Although we have never observed orifice plugging in our experiments, there may be some particle size fractionation occurring. Calculations indicate that there are only minor losses due to diffusion at these flowrates and tube diameters.

17. Subpicosecond Probing of Energy Transfer at Surfaces: Coupling of Adsorbate Vibrational Modes to Optically Excited Substrates

T.A. Germer, R.R. Cavanagh, E.J. Heilweil (PL), and J.C. Stephenson (PL)

The electronic excitations in solids that can be accessed by visible and ultraviolet radiation have recently been recognized as having the capacity to induce novel surface chemistry. To exploit and control these reactions fully, a better understanding of the energy transfer mechanisms that occur between the initially energized electrons in the substrate and the bonds of the adsorbed molecules is essential. Using subpicosecond pump-probe techniques, we have been able to follow the evolution of energy initially deposited in the substrate and to also address the time scale and mechanism involved in transferring energy to the adsorbate bonds.

The measurements were made with a half monolayer of CO bound to Pt(111). The surface is initially excited by a $100\text{ }\mu\text{J}$ pump pulse at 660 nm . A time-delayed picosecond probe pulse centered at 2106 cm^{-1} (15 cm^{-1} FWHM) was spectrally dispersed after reflecting from the surface. Experiments conducted in the presence of the CO adlayer revealed two effects. First, there was a spectrally uniform reduction in the IR reflectivity which could be quantitatively accounted for in terms of heating of the substrate. In addition, a marked shift in the CO stretch mode near 2106 cm^{-1} was apparent. This shift was attributed to activation of the 60 cm^{-1} frustrated translational mode of the Pt-CO bond. By examining the temporal dependence and extent of that shift, the time scale and magnitude of activation of the frustrated translational mode have been addressed.

Absorption of the visible pulse initially excites electrons in the metal, and on a 1.5 ps time scale the electrons equilibrate with the phonons, resulting in thermal heating of the crystal. In the first few picoseconds after the arrival of the excitation pulse, the electronic temperature is significantly greater than the surface lattice temperature. At these short time delays, the opportunity exists to determine whether the 60 cm^{-1} mode couples preferentially to the lattice or electronic modes of the platinum. Our results are explained if the coupling time for the frustrated translation is 1 ps or less for the lattice temperature, compared to approximately 1.5 ps for the electronic

temperature. The comparable magnitude of the two required coupling strengths indicates that both lattice and electronic degrees of freedom are equally capable of accounting for energy transfer between the substrate and the adlayer. The ability to establish limits on these coupling strengths will provide valuable guidance in future models of nonthermal surface processes.

Understanding and controlling the coupling of optical radiation to surface reactions is receiving considerable attention in catalysis, semiconductor processing, and solar energy conversion. Much of the current interest arises from the need to develop low temperature processing methods where the selective coupling of energy into surface layers represents an attractive method to achieve nonthermal phenomena. These measurements demonstrate the potential of ultrafast laser diagnostics for tracking electronically vs thermally driven interfacial processes.

18. Photodynamics of Mo(CO)₆/Si(111): Adsorption and Photofragmentation

L.J. Richter, S.A. Buntin, and P.M. Chu (Univ. of Maryland)

Optically driven surface reactions have received considerable attention due to their promise as new low temperature synthetic routes. Although a great deal of work on these systems has been reported, there is still little consensus on the details of the reaction mechanism(s). In an effort to clarify the steps in the photodeposition of metals on semiconductors, the photodynamics of Mo(CO)₆/Si(111) has been examined. Several new insights have emerged from studies of the adlayer and the ejected CO with Fourier-transform infrared (FTIR) and laser-induced fluorescence (LIF) techniques, respectively.

The FTIR work was performed with single external-reflection techniques, which are not usually applied to semiconductor substrates. While a novel application, external-reflection should be advantageous for *in situ* applications compared to the conventional multiple total-internal-reflection techniques. Under the conditions of this study, vibrational modes in the CO stretch region, which were polarized both parallel and perpendicular to the surface normal, were observed. These modes exhibited a large splitting, at all coverages from the submonolayer to the multilayer regime, as the result of strong dipole-dipole coupling between adjacent Mo(CO)₆ moieties. Based on the persistence of this splitting, it is clear that Mo(CO)₆ islanding is present at all coverages. This clustering can influence the subsequent photochemistry. FTIR was also used to follow the evolution of the adlayer during illumination. The experiment provided evidence for the photo-induced production of a number of distinct surface species, including Mo(CO)₅ and Mo_x(CO)_y, where x and y are not well-characterized. The distribution of products varied with the initial Mo(CO)₆ coverage.

Two velocity components were observed in state-resolved studies where LIF was used to detect the CO photofragments that are released following 266 nm irradiation of the surface. The relative contributions of the fast and slow components reflected a strong dependence on coverage. For studies with Mo(CO)₆ coverages of about 2-3 layers, it was found that the translational and

rotational degrees-of-freedom of the fast CO desorption component were highly excited relative to the surface temperature. For the slow component, studies of the surface temperature dependence indicated that the CO energy content was in quasi-equilibrium with the surface temperature. Based on these initial studies, the slow channel is thought to correspond to CO that has undergone multiple collisions within the adlayer before escaping the surface. Conversely, it appears that the fast channel results from CO that is directly ejected from the adlayer, with negligible interactions with the surface. The energy release in the fast component is significantly reduced relative to that of the isolated molecule, suggesting that the excited state loses a considerable amount of energy prior to dissociation. This quenching of optically prepared excited states will be key to understanding the viability of photochemical processing.

19. Metal/Non-Metal Transitions in High T_c Related Oxide Systems

S.W. Robey, R.V. Smilgys, L.T. Hudson, and B. Eichorn (Univ. of Maryland)

The high superconducting transition temperatures found in the copper-oxide based materials such as $Y_1Ba_2Cu_3O_{7-x}$ have stimulated interest in oxide systems in general. Of particular importance are questions concerning the doping of these materials and the nature of the electronic states formed by substitutions to form mixed oxide materials. In a collaboration with the University of Maryland, we are using synchrotron based photoemission to investigate the electronic structure of related model oxide systems. We have studied a series of Ti based compositional analogs $R_xBa_{1-x}TiO_3$, where $R = Y, La, \text{ and } Nd$, as well as the "parent" compound, $BaTiO_3$. These materials have the same structure as the cuprate superconductors, but without ordering of the R element and Ba into separate planes, and they undergo metal/non-metal transitions as a function of "R" substitution. The goal of this investigation is to understand the nature of this transition and the reason for the observation that the transition occurs at different substitution levels for different rare-earth substitutions. We have found that substitution of Y, La, or Nd for Ba in $BaTiO_3$ to form these compounds produces impurity states in what would be the band gap of $BaTiO_3$. The use of resonant photoemission effects identifies these as having predominantly Ti 3d character. This is in contrast to the high T_c cuprates for which doping produces states of predominantly O 2p character. Comparison with other systems suggests that the metal/non-metal transitions in these materials are due to disorder or "Anderson" localization effects. The strength of the resonant effect varies for the different materials, and is consistent with a concept in which different substitutions, R, affect the degree of Ti-O hybridization by competition for O 2p states. If this is correct this should influence the nature of the Ti 3d "impurity" states, which in turn, could affect the metal/non-metal transition point as a function of R element substitution.

20. Effects of Substrate Preparation on High T_c Thin Film Growth

R.V. Smilgys, S.W. Robey, and T.J. Hsieh (Univ. of Maryland)

Successful growth of high quality thin films of the cuprate superconductors for device fabrication may ultimately rest on the proper choice and preparation of substrates and/or buffer layers. Surface preparation procedures can drastically affect surface quality and thus T_c , J_c of the thin film, but almost no information is available concerning preparation requirements for many candidate substrate materials. For this reason, we are performing studies of the effect of substrate preparation on subsequent growth of "123" cuprate superconductor thin films. Thin films of $\text{Dy}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ are grown by reactive co-evaporation and studied *in situ* using surface sensitive techniques. We have concentrated on studies of the growth of thin films of $\text{Dy}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ on MgO. MgO is a potentially superior substrate for microwave applications but problems with surface reproducibility, coupled with the large lattice mismatch of $\sim 9\%$, have caused many groups to shift to other substrates such as LaAlO_3 . Our goal is to understand how various pre-treatments affect the MgO surface and how this in turn influences thin film growth. In particular, we have investigated the effect of pre-annealing the MgO substrate in oxygen. Previous work had indicated that this can produce superior films, but this is not universally observed. In fact, we observe film growth which is significantly degraded on pre-annealed substrates in terms of microstructure and, almost certainly, surface microwave resistance as well. We have observed a variety of surface effects upon pre-annealing such as surface roughening and segregation of Ca, which exists as a bulk impurity in MgO. We are investigating the role of each of these effects in influencing film growth.

21. Magnetic Thin Films

W.F. Egelhoff, Jr., M.T. Kief, M.D. Stiles, and G.L. Nyberg (Latrobe Univ., Australia)

The magnetic thin-film program consists of an experimental effort and a parallel theoretical effort.

(a) Magnetic Engineering Competence (Egelhoff, Kief, Nyberg): The objective of the experimental project is to provide industry with an understanding of how thin-film manufacturing processes affect magnetic and magnetoresistance properties in classes of magnetic thin films that have strong potential for application in commercial products. Two such commercial products are magnetic recording media (hard discs, floppy discs, etc.) and non-volatile computer memory chips. A new instrumental facility has been constructed for this work. The facility provides for film growth by both molecular-beam epitaxy and magnetron sputter deposition. The facility is equipped with an elaborate array of techniques for *in situ* structural and compositional characterizations of the thin films (x-ray photoelectron and Auger-electron spectroscopy, ion scattering spectroscopy, sputter-depth profiling, low-energy electron diffraction with spot-profile

analysis, reflection high-energy electron diffraction, spectroscopic ellipsometry, and scanning tunneling microscopy) and for *in situ* measurement in a superconducting magnet of film magnetic properties (spectroscopic Kerr effect and magnetoresistance). Our work this year consisted of a study of the thin-film growth modes of Co/Cu and Fe/Cu multilayer systems (which are strong candidates for a new generation of magnetoresistive memory elements in non-volatile computer memory chips). This work provided clearer understanding of the great complexity of these growth modes, as well as insight into how best to control and manipulate these growth modes for improved device performance.

(b) Theory of Exchange Coupling in Magnetic Thin Films (Stiles): The objective of the theoretical project is to understand antiferromagnetic coupling in magnetic sandwich structures and superlattices through non-magnetic spacer layers to optimize the Giant Magnetoresistance effect in devices. For these applications, it is desirable that the field required to reverse the magnetization be as small as possible; this field is determined by the strength of the antiferromagnetic coupling. One feature of the antiferromagnetic coupling is that it oscillates in sign as a function of the spacer-layer thickness, a behavior indicative of a possible Fermi-surface effect. To test whether the coupling is a Fermi-surface effect, we have calculated Fermi-surface properties for materials used as spacer layers. From the Fermi-surface properties, we have extracted the periodicities in the coupling strength and find these to be in good agreement with those measured with samples grown by molecular beam epitaxy. Samples grown by sputtering typically show a common oscillation period. Our results indicate that the periodicities in actual devices must depend on mechanisms of the film growth.

22. X-Ray Photoemission Studies of the Passivation of Gallium Arsenide Surfaces

T. Jach and M.J. Chester

One of the biggest impediments to the exploitation of gallium arsenide as a semiconductor material is our inability to prevent large deviations from the bulk electronic behavior at the surface. A number of schemes have been proposed recently to passivate the surface with a chemical layer of sulfur to bring its surface electronic structure closer to that expected from the bulk properties. We have investigated the effects of surface passivation using x-ray photoemission spectroscopy, Auger-electron spectroscopy, thermal desorption, and a new technique, grazing-angle x-ray photoemission spectroscopy. We have observed that oxidation of the surface is still able to take place following the passivation treatment, but the oxides form by diffusion of gallium and arsenic through the passivating layer. Oxides of different stoichiometries form at different depths. As these oxides are thermally evaporated, there is a change in surface electronic states that cause the Fermi level to change its position in the band gap. The use of grazing-angle x-ray photoemission allows us to determine the depth of different chemical constituents that have different core-electron binding energies through variation of the x-ray penetration depth.

23. New Inelastic De-excitation Processes at Ion-Bombarded Surfaces

J. Fine, K. Franzreb (Univ. of Kaiserslautern, Germany), and M. Yoshitake (National Research Institute for Metals, Japan)

Ion-beam-bombardment techniques are widely used not only to investigate the structure and composition of surfaces, but also to modify surfaces during thin-film growth and to promote chemical reactivity at surfaces during processing. The capabilities of these techniques are now limited by an incomplete understanding of the fundamental collisional phenomena involved. We have recently identified new inelastic collisional interactions that describe excitation, electron capture, and energy transfer.

We have investigated the electron emission spectra from several sodium halides following bombardment with neon or argon ions (in collaboration with Prof. M. Szymonski, Jagellonian University, Krakow). New features are found that are different from those observed with metal targets. Our new collisional de-excitation model involves excitation of a lattice sodium ion in a primary collision, production of an energetic (~ 100 eV) moving excited sodium ion, and collision of the sodium ion with lattice halogen ions. During such secondary collisions, the excited ion captures an electron, forms an excited atom, and then de-excites by emitting an electron. This electron-capture process can, in ionic solids, switch the Madelung potential from being attractive to repulsive, and can thus break chemical bonds and cause desorption of atoms from surfaces. Our new de-excitation process may be the dominant mechanism for chemical change in ionic solids; it is basic and has to be considered in the modeling of inelastic de-excitation processes in solids.

24. Electron Wave Packet Theory of Inelastic Resonant Tunneling: Quantum Wells, Adsorbed Atoms, and Scanning Tunneling Microscopy

J.W. Gadzuk

One of the most exciting and potentially revolutionary emerging areas of chemical processing at solid surfaces involves non-thermal, pulsed-laser excitation of valence electrons of a substrate material followed by controlled inelastic resonant scattering of these excited electrons by an atomic or molecular surface complex. Just as the ongoing quantum-state-specific, laser-induced-desorption experiments in the Surface Dynamical Processes Group are defining the experimental frontiers of this new capability for controlled atomic-scale surface processing, our complementary theoretical modeling and simulations are providing the understanding necessary for interpretation of existing data, for suggesting worthwhile directions of future experiments, and for critical predictions where definitive experiments are currently not feasible.

A major theoretical challenge for such laser-induced surface processes is the description of the excited, hot-electron dynamics given that the time-structure of the excitation pulse requires a

wave-packet description for the hot-electron time evolution. It is the inelastic resonant scattering of this wave packet by the surface molecule system that places localized quanta of energy into the reaction complex. We have developed theoretical methodology for numerical simulations of inelastic electron wave-packet scattering or tunneling and have tested the method on a number of atomic-scale systems of importance in surface chemistry. The common focus in the applications is vibrational excitation, possibly leading to bond-breaking dissociation or desorption. Such seemingly diverse problems as phonon excitation in GaAs quantum well tunneling, resonant desorption of adsorbed atoms or molecules, and site-specific tunneling spectroscopy with scanning tunneling microscopy have been addressed successfully with our theory.

25. Formation of a New Technical Committee on Surface Chemical Analysis by the International Organization for Standardization (ISO)

C.J. Powell

In response to a proposal from Japan, ISO formed Technical Committee 201 on Surface Chemical Analysis in 1992. As of October, 1992, ISO/TC 201 had ten full participating members (including the United States) and fifteen observer members. Guidance has been given in the preparation of formal documents defining the purpose, structure and activities of the new Committee. ISO/TC 201 will consider current standards produced by ASTM Committee E-42 on Surface Analysis as potential international standards, will establish liaison with the VAMAS Surface Chemical Analysis Technical Working Area and the IUPAC Working Group on Surface Analysis, will consider documents prepared by these international groups as potential international standards, and will develop new international standards itself. ISO/TC 201 will address instrument specifications, instrument operations, specimen preparation, data acquisition, data processing for qualitative analysis, data processing for quantitative analysis, reporting of results, terminology, and reference materials; it is thus expected to have a considerable impact on industrial usage of surface analysis throughout the world.

C. Outputs and Interactions
(Surface and Microanalysis Science Division)

1. Publications

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- Tanuma, S., Powell, C.J., and Penn, D.R., "Calculation of Electron Inelastic Mean Free Paths (IMFPs). IV. Evaluation of Calculated IMFPs and of the Predictive IMFP Formula TPP-2 for Electron Energies Between 50 and 2000 eV," *Surf. & Interface Anal.* (in press).
- Tanuma, S., Powell, C.J., and Penn, D.R., "Use of Sum Rules on the Energy-Loss Function for the Evaluation of Experimental Optical Data," *J. Electron Spectroscopy* (in press).
- Turner, S., Steel, E.B., Doorn, S.S., and Burris, S.B., "Analysis of Diffraction Patterns from Kaolinite Samples," PT 92-1 (1992).
- Turner, S., Burris, S.B., Steel, E.B., Doorn, S.S., and Phelps, J.M., "EDS Analysis, Mineral Identification and Diffraction Pattern Analysis," PT 92-2 (1992).
- Turner, S., Steel, E.B., Phelps, J.M., Windsor, E.S., Doorn, S.S., and Leigh, S.D., "Development of a Standard Reference Material for Analysis of Asbestos on Filters by TEM," in Proc. of the Electron Microscopy Society of America, 1706-1707 (1992).
- Verkouteren, R.M. and Klouda, G.A., "Factorial Design Techniques Applied to Optimization of AMS Graphite Target Preparation," *Radiocarbon* **34** (1992).

2. Talks

- Bennett, J.A., "GA Ion Sources in SIMS," 5th East Coast Workshop on SIMS, Somerset, PA, May 20, 1992. Invited
- Bennett, J.A., "Static SIMS-Monolayer Surface Analysis," 5th East Coast Workshop on SIMS, Somerset, PA, May 22, 1992.
- Bennett, J.A., "Methods for Increasing Parent Ion Signal Intensity from Bulk Organic Materials Analyzed with an Imaging Time-of-Flight Secondary Ion Mass Spectrometer," 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, DC, June 1, 1992.

- Bright, D.S., "Detectability of Objects in Noisy Images as a Function of Contrast, Size and the Rose Ratio, k ," MICRO 92 International Microscopy Conference and Exposition, Earl's Court Park Inn, London, England, July 9, 1992.
- Bright, D.S., "Basic Image Processing for the Microscopist," EMSA-MAS-MSJ Joint Meeting, Boston, MA, August 17, 1992. Invited
- Bright, D.S., "Visibility of Two Intermixed Phases as a Function of Grain Size and Signal-to-Noise: a Computer Simulation," EMSA-MAS-MSJ Joint Meeting, Boston, MA, August 18, 1992.
- Buntin, S., "State Resolved Studies of Substrated-Mediated Desorption," American Chemical Society Meeting, San Francisco, CA, April 8, 1992.
- Buntin, S., "State Resolved Studies of Laser Induced Desorption from Silicon Substrates," American Chemical Society Meeting, San Francisco, CA, April 10, 1992.
- Cavanagh, R.R., "Laser Spectroscopy of Surface Molecular Processes," Molecule-Surface Interactions: Theory and Experiment Workshop, Amsterdam, The Netherlands, November 15, 1991. Invited
- Cavanagh, R.R., "Time-Resolved Studies of Vibrational Relaxation: Model Compounds to Molecules on Surfaces," Analytical Chemistry Department, W.R. Grace, Columbia, MD, January 20, 1992.
- Cavanagh, R.R., "Laser Driven Surface Reactions: State Resolved Evidence for Non Thermal Mechanisms," University of California, San Diego, CA, March 10, 1992. Invited
- Cavanagh, R.R., "Time-Resolved Probes of Vibrational Energy Transfer: Model Compounds to Molecules at Surfaces," Dow Chemical Company, Detroit, MI, March 23, 1992. Invited
- Cavanagh, R.R., "Laser Probes of Surface Photoreactions: Carrier Induced Desorption," Michigan Catalysis Society Meeting, Detroit, MI, March 24, 1992. Invited
- Cavanagh, R.R., "Time-Resolved Probes of Surface Dynamics," 3rd Institute for Solid State Physics International Symposium on Dynamical Processes at Solid Surfaces, Tokyo, Japan, April 20, 1992.
- Cavanagh, R.R., "Time-Resolved Probes of Energy Transfer at Surfaces," Gordon Research Conference on Atomic and Molecular Interaction, New London, NH, July 21, 1992.

- Cavanagh, R.R., "Ultrafast Reactions at Surfaces: Opportunities and Limitations," European Science Foundation Workshop, Rhondorf, Germany, September 2, 1992.
- Chester, M.J., "Auger/XPS Study of UV/Ozone-Oxidized GaAs," STM Nanolithography Project Seminar, National Institute of Standards and Technology, Gaithersburg, MD, April 17, 1992.
- Chi, P., "Quantitative Depth Profiling of Diffused Deuterium at the Si/SiO₂ Interface," Fifth SIMS East Coast Workshop, Hidden Valley, PA, May 20, 1992.
- Chi, P., "Quantitative Secondary Ion Mass Spectrometry Depth Profiling of Diffused Deuterium in SIMOX Materials," ASMS Meeting, Washington, DC, May 31, 1992.
- Currie, L.A., "Mesons & On-Line Efficiency Monitoring in Low-Level Counting," University of Idaho, Idaho Falls, ID, November 7, 1991. Invited
- Currie, L.A., "Afterpulses from GM Counters: Experimental Strategies and Results," Gas Laboratory Uncertainty Evaluation Workshop, NIST, Gaithersburg, MD, March 19, 1992. Invited
- Currie, L.A., "Improved Atmospheric Understanding through Exploratory Data Analysis and Complementary Modeling: the Urban K-Pb-C System," Gordon Memorial Symposium, San Francisco, CA, April 7, 1992. Invited
- Currie, L.A., "Report of the Physicochemical Team for Laboratory Uncertainty Evaluation," The BOC Group Inc, Technical Center, Murray Hill, N.J., May 28, 1992. Invited
- Currie, L.A., "Total Quality Measurement," Conf. on Computer Applications in Analytical Chemistry, Jena, Germany, Plenary Lecture, August 27, 1992. Invited
- Duewer, D., "Presentation of Statistical Data Relating to Precision Study," FBI Forensic Science Research and Training Center, Quantico, VA, December 9, 1991.
- Duewer, D., "Chemometrics, Standard Test Data, and Spectroscopy," NIST Workshop at ANATECH-2, Lake Lanier Islands, GA, April 5, 1992.
- Duewer, D., "Final Report on Statistical Analysis of Data Relating to the Precision Study," Technical Working Group for DNA Analysis Methods, Quantico, VA, June 29, 1992.
- Duewer, D., "Current Chemometric Studies at NIST," Joint Statistical Meetings of American Statistical Association, Biometric Society and IMS, Boston, MA, August 13, 1992.

- Egelhoff, Jr., W.F., "Oscillations in Kerr Rotation and Antiferromagnetic Coupling in Fe/Cu/Fe Epitaxial Bilayers," International Workshop on Spin Valve Layered Structures, Madrid, Spain, September 9, 1991. Invited
- Egelhoff, Jr., W.F., "XPS Forward Scattering: A New Tool for Surface Structural Analysis," Department of Chemistry, University of Texas, Austin, TX, October 16, 1991. Invited
- Egelhoff, Jr., W.F., "XPS Forward Scattering: A New Tool for Surface Structural Analysis," Department of Chemistry, Texas A&M University, College Station, TX, October 17, 1991. Invited
- Egelhoff, Jr., W.F., "Antiferromagnetic Coupling in Fe/Cu/Fe and Co/Cu/Co Multilayers on Cu(111) and Cu(100)," American Physical Society Meeting, Indianapolis, IN, March 17, 1992.
- Egelhoff, Jr., W.F., "Antiferromagnetic Coupling in Fe/Cu/Fe and Co/Cu/Co Multilayers on Cu(111) and Cu(100)," International Magnetism Conference, St. Louis, MO, April 14, 1992.
- Egelhoff, Jr., W.F., "XPS Forward Scattering Studies of the Growth of Fe on Ag(100)," DoE Workshop on Surface Diffusion in the Growth of Materials, Santa Fe, NM, June 3, 1992. Invited
- Egelhoff, Jr., W.F., "XPS and Auger Forward Scattering: A Structural Probe for Magnetic Thin Films," International Symposium on Magnetic Thin Films, Lyon, France, September 9, 1992. Invited
- Etz, E.S., "Micro-Raman Spectroscopy of Diamond and DLC Films," Workshop on Characterizing Diamond Films, NIST-Gaithersburg, Gaithersburg, MD, February 28, 1992.
- Etz, E.S., "A Proposed Raman Standard for CVD Diamond," Research Division, Norton Diamond Film, Northboro, MA, May 8, 1992.
- Etz, E.S., "Rare Earth Fluorescence in Raman Microprobe Spectra of Glasses and Ceramics," 26th Annual Meeting of the Microbeam Analysis Society, Boston, MA, August 18, 1992.
- Fine, J., "Evaluation of Sputter-Induced Interface Broadening Processes in Multilayered Materials," Fourth Topical Conference on Quantitative Surface Analysis, Eatonville, WA, November 9, 1991. Invited
- Fine, J., "Collisionally Excited Sputtered Al Atoms: A Molecular Dynamics Trajectory Calculation," American Vacuum Society Meeting, Seattle, WA, November 11, 1991.

- Fine, J., "Imaging of Surface Microroughness by Scanning Scattering Microscopy," American Vacuum Society Meeting, Seattle, WA, November 14, 1991.
- Fine, J., "A NIST Marker-Layer Standard Reference Material for Depth Profile Analysis," American Vacuum Society Meeting, Seattle, WA, November 14, 1991.
- Fine, J., "Electron Stimulated Desorption Mechanisms in Insulators," Department of Physics, University of Kaiserslautern, Kaiserslautern, Germany, March 13, 1992. Invited
- Fine, J., "Electron Stimulated Desorption Mechanisms in Insulators," Interdisciplinary Conference on Dielectrics, Antibes, France, March 24, 1992. Invited
- Fletcher, R.A., Verkouteren, R.M., Wight, S.A., Miller, J.R., and Thornberg, S.M., "Measurements Associated with Using Small Orifices as Controlled Leaks in Aerosol and Particle Free Systems," Poster Presentation at the 10th Annual Meeting of the American Association of Aerosol Research, Traverse City, MI, October 8, 1991.
- Gadzuk, J.W., "The Early Days of Quantum Mechanics in Modern Surface Science," Workshop on Surface Science: Past, Present and Future, Cornell University, Ithaca, NY, December 16, 1991.
- Gadzuk, J.W., "Single Atom Point Source for Electrons: Field Emission Resonance Tunneling in an STM World," American Physical Society Meeting, Indianapolis, IN, March 16, 1992.
- Gadzuk, J.W., "Some Current Theoretical Insights on DIET," Fifth International Workshop on Desorption Induced by Electronic Transitions, Taos, NM, April 1, 1992. Invited
- Gadzuk, J.W., "Desorption Induced by Electronic Transitions: What's New?," IBM Almaden Research Laboratory, San Jose, CA, April 6, 1992. Invited
- Gadzuk, J.W., "Hot Electrons: The Key to Surface Photochemistry?," American Chemical Society Meeting, San Francisco, CA, April 7, 1992. Invited
- Gillen, J.G., "Spatially Resolved Microbeam Mass Spectrometry," Departments of Analytical and Physical Chemistry, University of Delaware, Newark, DE, March 2, 1992. Invited
- Gillen, J.G., "Microbeam Mass Spectrometry," Department of Chemistry, Montana State University, March 4, 1992. Invited
- Gillen, J.G., "Imaging Detectors for Ion Microscopy," 5th East Coast Workshop on Secondary Ion Mass Spectrometry, Hidden Valley, PA, May 20, 1992.

- Gillen, J.G., High Dynamic Range Mesa Depth Profiling," 5th East Coast Workshop on Secondary Ion Mass Spectrometry, Hidden Valley, PA, May 21, 1992.
- Gillen, J.G. and Zeissler, C.J., "Localization of Labeled Compounds in Human Hair Using SIMS," 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D.C., June 1, 1992.
- Gillen, J.C., "Molecular Imaging SIMS: Limitations and Future Prospects," ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D.C., June 1, 1992.
- Gillen, J.G., "Application of Secondary Ion Mass Spectrometry for Elemental and Molecular Microanalysis of Biological Materials," 33rd ORNL-DoE Conference on Analytical Chemistry in Energy Technology, Oakridge, TN, September 30, 1992. Invited
- Hudson, L.T., "Resonant Photoemission and Core-Level Study of Single Crystal BaTiO₃," American Vacuum Society Meeting, Seattle, WA, November 13, 1991.
- Hudson, L.T., "A Photoelectron Spectroscopic Study of Barium Titanate," Department of Physics Colloquium, University of Texas, El Paso, TX, December 6, 1991.
- Jach, T., "X-Ray Standing Waves," Synchrotron Radiation Instrumentation Collaborative Access Team Workshop, Argonne National Laboratory, Argonne, IL, June 19, 1992.
- Jach, T., "Depth Dependence of Sulfur and Oxides on Passivated GaAs," Gordon Conference on Electron Spectroscopy, Wolfboro, NH, July 14, 1992.
- Kief, M.T., "Epitaxial Growth of Fe and Co on Cu(111)," American Physical Society Meeting, Indianapolis, IN, March 16, 1992.
- Kief, M.T., "Thickness Dependent Curie Temperature of Epitaxial Ultrathin Films," American Physical Society Meeting, Indianapolis, IN, March 16, 1992.
- Klouda, G.A., "Electronegative Impurities in the NSG-V Working Standard," Meeting of the GLUE Panel, May 27, 1991.
- Kurtz, R.L., "Photoelectron Imaging of Fermi Surfaces," 7th National Conference on Synchrotron Radiation Instrumentation, Louisiana State University, Baton Rouge, LA, October 29, 1991. Invited
- Kurtz, R.L., "Photoelectron Angular Distributions from Clean and Absorbate-Covered Ru(0001)," American Vacuum Society Meeting, Seattle, WA, November 12, 1991.

- Marinenko, R.B., "The Image is the Thing: A Practical Approach to the Application and Acquisition of Digital X-ray Mapping," Missouri MAS, Columbia, MO, May 6, 1992. Invited
- Marinenko, R.B., "The Image is the Thing: A Practical Approach to the Application and Acquisition of Digital X-ray Mapping," MSSEM/CMAS/RMMS Spring Symposium, USGS Denver Fed. Cen., May 7, 1992. Invited
- Marinenko, R.B., "The Image is the Thing: A Practical Approach to the Application and Acquisition of Digital X-ray Mapping," New Mexico Microbeam Users Group, Albuquerque, NM, June 3, 1992. Invited
- Marinenko, R.B., "The Image is the Thing: A Practical Approach to the Application and Acquisition of Digital X-ray Mapping," No. Cal. Soc. of Elect. Micros., Palo Alto, CA, June 4, 1992. Invited
- Marinenko, R.B., "The Image is the Thing: A Practical Approach to the Application and Acquisition of Digital X-ray Mapping," So. Cal. Micro. Anal. Soc., Los Angeles, CA, June 4, 1992. Invited
- Marinenko, R.B., "Compositional Mapping with Electron Beam Instruments," Thermal Spray Workshop, NIST, July 20, 1992.
- Marinenko, R.B., "Quantitative Electron Probe Microanalysis of Lithium-Aluminum-Borate Glasses: A Feasibility Study," 27th Ann. Meeting of the Microbeam Anal. Soc., Boston, MA, August 17, 1992.
- Newbury, D.E., "Microanalysis to Nanoanalysis: Measuring Composition at High Spatial Resolution," Keynote Paper, Materials Characterization Conference and Exposition, United Technologies Research Center, East Hartford, CT, October 30, 1991. Invited
- Newbury, D.E., "Compositional Mapping at the Micrometer Scale - and Finer," NIST Symposium on Science, Technology, and Competitiveness, (90th Anniversary of NIST) NIST, Gaithersburg, MD, November 15, 1991. Invited
- Newbury, D.E., "Elemental Analysis at High Spatial Resolution AND Trace Sensitivity," Materials Science and Engineering Laboratory, NIST, Gaithersburg, MD, January 6, 1992. Invited
- Newbury, D.E., "A Comparison of $f(rz)$, Monte Carlo, and ZAF Calculations for Thin Films," Scanning 92, Atlantic City, NJ, April 1, 1992 Invited

Newbury, D.E., "Materials Science and Engineering," Ridgeview Intermediate School Career Day, Gaithersburg, MD, April 3, 1992.

Newbury, D.E., "Microanalysis to Nanoanalysis: Measuring Composition at High Spatial Resolution," Department of Chemistry, University of Massachusetts, Amherst, MA, May 5, 1992. Invited

Newbury, D.E., "Microanalysis to Nanoanalysis: Measuring Composition at High Spatial Resolution," NIST Workshop on Nanostructured Materials, Gaithersburg, MD, May 14, 1992. Invited

Newbury, D.E., "SIMS Imaging for the Microcharacterization of Aluminum-Lithium Alloys," 5th East Coast Workshop on Secondary Ion Mass Spectrometry, Hidden Valley, PA, May 22, 1992.

Newbury, D.E., "Recent Developments in Microbeam Analysis at NIST," the University of Oxford, Department of Materials Science, Oxford, England, July 2, 1992. Invited

Newbury, D.E., "Trace Nanoanalysis by Parallel Detection Electron Energy Loss Spectrometry," University of Cambridge, Department of Materials Science and Metallurgy, Cambridge, England, July 3, 1992. Invited

Newbury, D.E., "Image Processing for Compositional Mapping by Microbeam Analysis," Micro 92, international conference organized by the Royal Microscopical Society, London, England, July 9, 1992. Invited

Newbury, D.E., "Compositional Mapping by Electron Probe Microanalysis," Invitational Workshop on Future Directions in Microscopy and Imaging, organized by the Electron Microscopy Society of America, Southboro, MA, August 15, 1992. Invited

Newbury, D.E., "Predicting Resolution in Backscattered Electron SEM Images from Monte Carlo Calculations of the Interaction Volume," Joint Conference of the Microbeam Analysis Society/Electron Microscopy Society of America, Boston, MA, August 20, 1992.

Powell, C.J., "Activities of the ASTM Committee E-42 on Surface Analysis," Fourth European Conference on Applications of Surface and Interface Analysis, Budapest, Hungary, October 14, 1991.

Powell, C.J., "The NIST X-Ray Photoelectron Spectroscopy Database," Fourth European Conference on Applications of Surface and Interface Analysis, Budapest, Hungary, October 14, 1991.

- Powell, C.J., "Evaluation of a Formula for Predicting Inelastic Mean Free Paths of 50-2000 eV Electrons in Solids," Fourth European Conference on Applications of Surface and Interface Analysis, Budapest, Hungary, October 14, 1991.
- Powell, C.J., "Evaluation of a Formula for Predicting Inelastic Mean Free Paths of 50-2000 eV Electrons in Solids," American Vacuum Society Meeting, Seattle, WA, November 15, 1991.
- Powell, C.J., "Reference Data and Reference Materials for Surface Analysis," International Symposium on Prestandards Research for Advanced Materials, Toranomon Pastral, Minato-ku, Tokyo, Japan, December 17, 1991. Invited
- Powell, C.J., "Calibration of the Electron Binding Scales of X-Ray Photoelectron Spectrometers," Versailles Project on Advanced Materials and Standards Meeting, Hakone, Japan, December 18, 1991.
- Powell, C.J., "Progress in Quantitative AES and XPS: The Role of Matrix Factors," 14th Symposium on Applied Surface Analysis, University of Michigan, Ann Arbor, MI, June 11, 1992. Invited
- Powell, C.J., "Electron Inelastic Mean Free Paths in Organic Compounds for Energies Between 50 and 2000 eV," Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH, July 14, 1992.
- Powell, C.J., "The Role of Matrix Factors in Quantitative Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," Seventh International Conference on Quantitative Surface Analysis, Guildford, UK, September 8, 1992. Invited
- Powell, C.J., "Formation of Technical Committee 201 on Surface Chemical Analysis by the International Organization for Standardization," Seventh International Conference on Quantitative Surface Analysis, Guildford, UK, September 9, 1992.
- Richter, L.J., "State-Resolved Studies of Laser-Induced Reactions on Si Surfaces," IBM T. J. Watson Research Center, Yorktown Heights, NY, February 3, 1992.
- Richter, L.J., "State-Resolved Studies of the Photodissociation of Mo(CO)₆ on Si(111) 7x7," American Physical Society Meeting, Indianapolis, IN, March 16, 1992.
- Richter, L.J., "State-Resolved Studies of Laser-Induced Reactions on Si Surfaces," Fifth International Workshop on Desorption Induced by Electronic Transitions, Taos, NM, April 2, 1992.

- Robey, S., "Resonant Photoemission Investigations of the Electronic Structure of $R_1\text{Ba}_2\text{Ti}_3\text{O}_x$," American Physical Society Meeting, Indianapolis, IN, March 16, 1992.
- Robey, S., "Electronic Structure of $R_1\text{Ba}_2\text{Ti}_3\text{O}_{9-x}$ with $R=\text{Y}, \text{La}, \text{Nd}$," Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH, July 14, 1992.
- Simons, D.S., "Factors Influencing Quantitative SIMS Using a Microfocused Ga Ion Beam and TOF-MS," Eighth International Conference on Secondary Ion Mass Spectrometry, Amsterdam, The Netherlands, September 19, 1991.
- Simons, D.S., "Quantitative Depth-Profiling of Ion-Implanted Silicon by SIMS, RBS, and Thermal Neutron Depth Profiling," Fourth Topical Conference on Quantitative Surface Analysis, Eatonville, WA, November 9, 1991. Invited
- Simons, D.S., "Searching for Isotopic Anomalies by Mass Spectrometry," NIST Computing and Applied Mathematics Laboratory Review Panel, March 24, 1992. Invited
- Simons, D.S., "Ion Detectors for SIMS," Fifth East Coast Workshop on Secondary Ion Mass Spectrometry, Somerset, PA, May 20, 1992. Invited
- Simons, D.S., "Transition Metal Ion Implants in InGaAs Measured by Secondary Ion Mass Spectrometry," Microbeam Analysis Society, Boston, MA, August 18, 1992.
- Small, J.A., "Accuracies Associated with the Automated Electron Probe Analysis of Particulate Populations," Microbeam Analysis Society, Boston, MA August 19, 1992. Invited
- Smilgys, R., "Auger Electron Spectroscopy Study of DyBaCuO Films Grown by Coevaporation," American Physical Society Meeting, Indianapolis, IN, March 17, 1992.
- Stiles, M.D., "Ballistic Transport Across Interfaces," Workshop on Epitaxy, Interfaces, Defects and Processing of Electronic and Photonic Materials, Pittsburgh, PA, November 6, 1991. Invited
- Stiles, M.D., "Single Electron Charging Effects," Pennsylvania State University, State College, PA, November 8, 1991. Invited
- Stiles, M.D., "Fermi Surface Nesting in Metallic Heterostructures," American Physical Society Meeting, Indianapolis, IN, March 17, 1992.
- Stiles, M.D., "Heterojunction Devices," American Physical Society Meeting, Indianapolis, IN, March 17, 1992.

- Stiles, M.D., "Fermi Surface Extrema in Metallic Heterostructures," 4th Annual Workshop on Recent Developments in Electronic Structure Algorithms, North Carolina State University, Raleigh, NC, May 16, 1992.
- Stiles, M.D., "Fermi Surface Nesting in Metallic Heterostructures," Symposium on Magnetic Ultra Thin Film, Multilayers, and Surfaces, Lyon, France, September 9, 1992.
- Turner, S., "Aspects of a New Transmission Electron Microscopy Method for AHERA," National Asbestos Conference Meeting, Pittsburgh, PA, April 9, 1992.
- Turner, S., "Aspects of QA for Analysis of Airborne Asbestos," Johnson Conference Meeting, Johnson, VT, July 16, 1992.
- Turner, S., Steel, E.B, Phelps, J.M, Windsor, E.S., Doorn, S.S, and Leigh, S.D., "Development of a Standard Reference Material for Analysis of Asbestos on Filters by TEM." EMSA/MAS Meeting, Boston, MA, August 19, 1992.
- Velapoldi, R.V., "Chemical Research in CSTL," University of Virginia, Charlottesville, VA, November 8, 1991.
- Velapoldi, R.V., "Measurement Progress and Quality Assurance," and "Results of Analyses and Process Implications," Department of Defense, Orlando, FL, January 31, 1992.
- Velapoldi, R.V., "Chemistry in the Nineties," University of Virginia/National Science Foundation Undergraduate Research Program, NIST, Gaithersburg, MD July 24, 1992.
- Wight, S.A. and Divita, F., "Performance of the Micro-Orifice Uniform Depository Impactor Collecting Ambient Aerosol from the Philadelphia Area for Elemental Analysis," Poster Presentation at the 10th Annual Meeting of the American Association of Aerosol Research, Traverse City, MI, October 8, 1991.
- Wight, S.A., and Divita, F., "Analysis of Philadelphia Aerosol," Joint Meeting of the Electron Microscopy Society of America, Microbeam Analysis Society, and the Microscopical Society of Canada, Boston, MA, August 19, 1992.
- Zeissler, C.J., "Imaging with Bubble Detectors," 10th International Conference on Solid State Dosimetry, Washington, D.C., July 17, 1992.
- Zeissler, C.J., "Particle Preparation for Materials Analysis," Microbeam Analytical Society, Boston, MA, August 17, 1992. Invited

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

None

4. Patent Awards and Applications

None

5. SRM Activities

SRM 1867 Commercially Uncommon Asbestos
SRM 1868 Quantitative Asbestos
SRM 2135 Ni/Cr Multilayer
SRM 2063 Thin Film Glass Standard
SRM 2064 Thin Film Glass Standard
SRM Electron Spectrometry Energy Scale Standards

6. SRD Activities

SRD 20 X-Ray Photoelectron Spectroscopy
SRD Desktop Spectrum Analyzer

7. Calibrations

None

8. Committee Assignments

S. Buntin

Office of Naval Research Postdoctoral Review Committee

R.R. Cavanagh

Gordon Research Conferences - Dynamics of Gas/Surface Interactions ('93) (Vice President)

J. Fine

Sub-committee on Standard Reference Materials, ASTM Committee E-42 on Surface Analysis (Chairman)

L.A. Currie

IUPAC Commission V.1 (General Aspects of Analytical Chemistry) (Titular member)
IUPAC Working Group on Chemometrics
IUPAC Commission on Environmental Analytical Chemistry
Commission on Environmental Analytical Chemistry, IUPAC
International Radiocarbon Conference on "Environmental Science" (Chairman)
Technical Issues Team (DoC-QA) (Leader)
NSF Advisory Board for WHOI Accelerator Laboratory (Chairman)
American Statistical Association, Committee for the "Chemostatistics Award"
NIST Consultative Group for ISO/TAG4 Working Group on "Guide to the Expression of Uncertainty in Measurement"
CSTL Long-range planning committee on "Process Modeling and Simulation"
IAEA: Multivariate Exploration of Data Structure and Quality
ANSI Committee, Yankee Atomic Electric Co., State of Arizona-Detection and Regulation (Advisor)

D.L. Duewer

North American Chapter of the International Chemometrics Society (Secretary)

E.S. Etz

ASTM E-13 Molecular Spectroscopy
ASTM E-13.08 Raman Spectroscopy

J. Fine

Sub-committee on Standard Reference Materials, ASTM Committee E-42 on Surface Analysis (Chairman)

R.A. Fletcher

IES Working Group 014 - Calibration of Airborne Particle Counters

J.W. Gadzuk

Advisory Editorial Board, "Progress in Surface"
International Advisory Committee, 7th International Conference on Vibrations at Surfaces
CSTL Colloquium Committee
NIST Information Resource Center (Subject Specialist Consultant)

T. Jach

Organizing Committee for the 8th Annual Conference on Synchrotron Radiation Instrumentation

G.A. Klouda

Division 837 Safety Committee

R.B. Marinenko

Microbeam Analysis Society (Director)

R.L. Myklebust

ASTM E-2 Emission Spectroscopy

ASTM E-2.04 Standard Reference Material

D.E. Newbury

ASTM E-42 Surface Analysis

NIST Colloquium Committee

C.J. Powell

ASTM Committee E-42 on Surface Analysis, Member of Executive Committee, International Liason, Member of US Technical Advisory Group for ISO/TC 201 on Surface Chemical Analysis

Technical Committee 201 on Surface Chemical Analysis of the International Organization for Standardization (Chairman)

Surface Chemical Analysis Technical Working Area, Versailles Project on Advanced Materials and Standards (US representative and Vice-Chairman)

Applied Surface Science Division, International Union of Vacuum Science, Technique, and Applications (Chairman)

Program Committee, 12th International Vacuum Congress and 8th International Conference on Solid Surfaces

Organizing Committee, 4th Topical Conference on Quantitative Surface Analysis (Chairman)

D.S. Simons

ASTM E-42 Surface Analysis

ASTM E-42.06 Secondary Ion Mass Spectrometry

ASTM E-42.09 Standard Reference Material

J.A. Small

Microbeam Analysis Society (Secretary)

ASTM D-22 Sampling and Analysis of Atmospheres

E.B. Steel

ASTM D-22 Sampling and Analysis of Atmospheres

ISO/TC 146/SC3/WGI International Standards Organization Committee

R. A. Velapoldi

ASTM E-11 on Statistical Methods

ASTM E-13 on Molecular Spectroscopy

ASTM E-13.06 on Molecular Luminescence

ASTM E-13.06.01 on Presentation of Corrected Fluorescence Spectra
ASTM E-13.06.02 on Recommended Practices on Molecular Fluorescence Spectroscopy
DoE Review Committee

9. Editorships

L.A. Currie

CRC Press Chemometrics Series (Advisory Editor)

J.W. Gadzuk

Progress in Surface (Advisory Editorial Board)

C.J. Powell

Applications of Surface Science (Editorial Board)

Surface and Interface Analysis" (Editorial Board)

Methods of Surface Characterization (Editorial Board)

Journal of Electron Spectroscopy (Editorial Board)

Surface Science Spectra (Editorial Board)

10. Seminars

October 11, 1991

U. Hofer, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY, "Surface Diffusion and Desorption Kinetics of Hydrogen on Silicon." (Division Sponsor: R.R. Cavanagh)

October 18, 1991

J. Harris, Institut für Festkörperforschung, Jülich, Germany, "Methane Dissociation at Metal Surfaces: Theory Meets Experiment." (Division Sponsor: J.W. Gadzuk)

November 18, 1991

A. Jablonski, Polish Academy of Sciences, Warsaw, Poland, "Electron Transport in the Surface Region of Solids: Impact on Quantitative Electron Spectroscopies." (Division Sponsor: C.J. Powell)

November 22, 1991

P. Geladi, Research Group for Chemometrics, University of Umea, Umea, Sweden, "Multivariate Image Analysis in Chemical Applications: Statistical and Visual Diagnostics." (Division Sponsor: D.L. Duewer)

December 13, 1991

M.T. Kief, National Institute of Standards and Technology, Gaithersburg, MD, "Magneto-optic Studies of Two-Dimensional Ferromagnetism." (Division Sponsor: W.F. Egelhoff)

December 18, 1991

C. Brenninkmeijer, Department of Scientific and Industrial Research, Lower Hutt, New Zealand, "¹⁴C ¹³C and ¹⁸O in Atmospheric Carbon Monoxide: A Unique Tool." (Division Sponsor: R.M. Verkouteren)

April 14, 1992

L. Connell, Department of Chemistry, University of California, Los Angeles, CA, "Structural Studies of Hydrogen-Bonded Clusters Using Rotational Coherence Spectroscopy." (Division Sponsor: L.J. Richter)

April 17, 1992

T. Rahman, Department of Physics, Kansas State University, Manhattan, KS, "Atoms Sliding, Sloshing, Vibrating and Disordering at Metal Surfaces--a Molecular Dynamics Study." (Division Sponsor: R.R. Cavanagh)

May 4, 1992

J.M. Conny, Chemistry Department, University of Colorado, "Use of Isotopes to Study Sources and Reactions of Chemical Species in the Atmosphere." (Division Sponsor: L.A. Currie)

June 8, 1992

O. Kvalheim, Department of Chemistry, University of Bergen, Bergen, Norway, "Multivariate Data Analysis: New Developments and Applications in Chemistry." (Division Sponsor: R.A. Velapoldi)

June 22, 1992

J. Mitchell, Atomic Energy Authority, Division of Energy, United Kingdom, "Summary of Work Being Done by the AEA." (Division Sponsor: R.A. Fletcher)

11. Conferences/Workshops Sponsored/Co-Sponsored

November 8-9, 1991

4th Topical Conference on Quantitative Surface Analysis, Eatonville, WA

May 20-23, 1992

5th East Coast Workshop on Secondary Ion Mass Spectrometry

12. Other

a. Faculty Appointment

R.L. Kurtz

Associate Professor of Physics and Astronomy, Louisiana State University, Baton Rouge,
LA

T.E. Madey

Professor of Surface Science, Rutgers University, Piscataway, NJ

R.L. Stockbauer

Professor of Physics and Astronomy, Louisiana State University, Baton Rouge, LA

b. NIST Standard Reference Ozone Photometer

Company or Organization

Boeing Company

Dept. of the Air Force

Environment Canada, EPS

Environment Canada, AQB

EPA - SRP #7

Fusion Semiconductor Systems

IN USA Incorporated

Ministry of Environment - SRP #12

NIST - SRP #0

NOAA

Xerox Corporation

VIII. Thermophysics Division (838)

Richard F. Kayser, Chief

A. Division Overview

The Thermophysics Division conducts research in three major areas: the thermophysical properties of fluids and fluid mixtures, the thermophysical properties of solids at high temperatures (above 1500 K), and the measurement of pressure, vacuum, and leak rate. The thermophysical properties of fluids and fluid mixtures are essential to the well-being of the chemical and related industries to ensure equity in trade, innovation in process design and control, and improvements in equipment performance. The properties of solids at high temperatures play a key role in designing and fabricating high-performance materials for use in spacecraft and nuclear reactors. Accurate measurements of pressure, vacuum, and leak rate are vital in the chemical process, semiconductor, energy and power, automotive, aerospace, and defense-related industries for process control and product quality assurance.

The research on fluid properties comprises experimental, theoretical, and computer simulation studies of the equilibrium, transport, and interfacial properties of pure fluids and fluid mixtures. The experimental research entails the development of new, state-of-the-art measurement techniques and the provision of highly accurate thermophysical properties data for carefully selected pure fluids and fluid mixtures. The fluids studied are representative of broad classes encountered in many industries. In synergism with the experimental programs, the Division critically evaluates and correlates thermophysical properties data and conducts research on fundamental theoretical models, new concepts and phenomena, and predictive algorithms. The results of these efforts appear as conventional correlations and tables, and more recently, as predictive computer codes.

The program on high-temperature solids focuses on the development and use of millisecond and microsecond techniques to measure the thermophysical properties of solids under conditions where conventional steady-state methods fail. Materials studied include high-temperature electrical conductors and metallic composites. Important products of this research include reliable thermophysical properties data and high-temperature Standard Reference Materials.

The goals of the research on pressure and vacuum are to develop new and more accurate measurement methods and concepts (e.g., pressure fixed points) and to improve the U.S. national measurement standards for pressure, vacuum, and leak rate. The pursuit of these goals requires in-depth investigations of pressure and vacuum instrumentation, including piston gages, manometers, capacitance diaphragm gages, ionization gages, spinning rotor gages, and partial pressure analyzers. The Division performs calibration and special test services for pressure (from 10^{-7} to 10^9 Pa) and leak rate (from 10^{-14} to 10^{-8} mol/s) and offers precision measurement workshops on the measurement of pressure, vacuum, and leak rate. There continue to be numerous collaborations and interactions with equipment manufacturers, users, and other

laboratories to provide traceability and to improve the accuracy of pressure, vacuum, and leak-rate measurements throughout the United States.

During the past year, the Division continued its comprehensive program on the thermophysical properties of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) alternatives. This program is part of the national and international effort to replace CFCs and HCFCs with non-ozone-depleting alternatives in accordance with the revised Montreal Protocol and the 1990 Amendments to the Clean Air Act. CFCs and HCFCs are pervasive in modern society as working fluids in small and large-scale air-conditioning and refrigeration equipment, as blowing agents in the production of foams and insulations, and as solvents and degreasers for metal parts and electronic circuit boards. The objectives of the program are to acquire highly accurate thermophysical properties data for promising alternative refrigerants and refrigerant mixtures and to develop models to predict these thermophysical properties. These data and models are essential to screen mixtures for diverse applications, to implement the new fluids in existing equipment, and to design and optimize new equipment. The most promising alternative refrigerants include incompletely fluorinated ethane-, methane-, and propane-based compounds and their mixtures.

The computer package, REFPROP, has become the principal vehicle for disseminating the Division's research on alternative refrigerants. The current version calculates the equilibrium and transport properties of 26 alternative refrigerants and mixtures with as many as five components. Engineers in the air conditioning and refrigeration industry use REFPROP to design and optimize equipment to operate reliably and efficiently with alternative working fluids. To date, the NIST Standard Reference Data Program (SRDP) has sold more than 200 copies of REFPROP, which makes REFPROP one of the most popular databases that SRDP distributes. The Air Conditioning and Refrigeration Institute and the Electric Power Research Institute have adopted REFPROP as the source of thermophysical properties data for their Alternative Refrigerants Evaluation Program.

Future efforts in the area of alternative refrigerants will concentrate more on the identification and characterization of alternatives for the HCFCs, especially HCFC-22 (CHF_2Cl). The emphasis will be almost entirely on mixtures, since there are no obvious pure fluids that could serve as substitutes for the fluids currently in use. To help industry replace the HCFCs, it will be necessary to develop more accurate methods to predict the equilibrium and transport properties of mixtures, especially mixtures that contain both polar and non-polar pure alternative refrigerants. The development of accurate models for mixtures of chemically and/or physically dissimilar components is an important long-range goal of the overall program on thermophysical properties.

The study of natural gas mixtures is another area of significant emphasis. The objective of this work is to provide the natural gas industry and the rate payer with the validated property data and models needed for custody-transfer transactions and for the design, control, and optimization of gas processes. Recently, the Division completed its part in a major

international effort sponsored by the Gas Research Institute. This long-term project led to a validated set of PVT data for natural gas mixtures in the major region of custody-transfer transactions. A related project for the Gas Processors Association involves measurements of the densities of a number of natural gas liquid components and their mixtures. The purpose of this work is to improve the accuracy of the volume correction factors used in the custody transfer of natural gas liquids. The aim of yet a third program is to study the quality of natural gas. Current efforts are concentrating on the physicochemical behavior of trace contaminants, such as halogenated hydrocarbons, in natural gas and natural gas pipelines. A longer-term goal is to devise methods to separate the contaminants from the pipelines.

A new collaborative project with the Process Measurements Division is focusing on an exciting new technology for destroying hazardous and toxic wastes. Called Supercritical Water Oxidation, this technology exploits the fact that organic and certain inorganic materials can be hydrolyzed and oxidized to mostly innocuous products under the relatively mild conditions of water above its critical point ($T_c = 647 \text{ K}$, $P_c = 22 \text{ MPa}$). The Division's recent research on NaCl , CO_2 , and N_2 in water at high temperatures provides an excellent starting point for future efforts to develop more comprehensive models for multicomponent solutions containing salts, CO_2 , air, oxygen, and organic and inorganic compounds; the phase behavior of such solutions from room temperature to above the critical point is especially crucial for the design of SCWO processes. In the long run, it will be necessary to develop models that incorporate both ionic association and chemical reactions.

As another major activity, the Division maintains the Fluid Mixtures Data Center and the Polar Fluids Data Project for the NIST Standard Reference Data Program (SRDP). The Fluid Mixtures Data Center provides timely technology transfer of thermophysical properties data and models to the chemical process industry. The Data Center compiles and evaluates data on the thermodynamic and transport properties of fluids and fluid mixtures and produces such well-known microcomputer data bases as MIPROPS and DDMIX. Most recently, the Data Center has created the computer package, SUPERTRAPP, which enables the user to calculate phase equilibria, single-phase properties, and transport properties for 116 pure fluids and fluid mixtures with as many as 20 components. MIPROPS, DDMIX, and SUPERTRAPP are all available through the SRDP. Future efforts in the Fluid Mixtures Data Center will focus on structure-based modeling, which will involve the development of techniques for estimating chemical and physical properties based on molecular information alone. The Polar Fluids Data Project encompasses much of the Division's work on water and aqueous systems, including efforts through the American Society of Mechanical Engineers and the International Association for the Properties of Water and Steam to develop new scientific and industrial formulations for the thermophysical properties of water and steam. When adopted in 1994, the new scientific formulation will replace the internationally accepted "NBS Steam Tables" developed in the Division in the early 1980s. The Polar Fluids Data Project is also responsible for the predictive computer package, REFPROP, described above.

The construction of eight new thermophysical properties apparatus progressed well during the past year under the sponsorship of the Department of Energy. The current five-year program is the continuation of an intensive effort begun in the early 1980s to improve the thermophysical property measurement capabilities of the U.S. The new apparatus will extend the existing state of the art for property measurements and make it possible to study complex fluid systems that are inaccessible at present, including highly polar, electrically conducting, and reactive fluids. The measurement capabilities under development include new apparatus for transport properties, thermodynamic properties, phase equilibria properties, and dielectric properties. Several additional projects also are underway aimed at developing novel capacitive and electromagnetic resonance techniques for the on-line detection of phase transitions for applications in the chemical process industry.

Efforts to establish practical high-temperature reference points continued during the past year with the completion of measurements of the radiance temperature of tungsten at its melting point at six wavelengths in the range 400-900 nm. The results on tungsten are especially significant since tungsten has the highest melting point (3695 K) among the metallic elements. Also completed was a new method for measuring the thermal conductivity of electrical conductors at high temperatures. The new method uses a high-speed spatial scanning pyrometer developed in-house to record the transient temperature distribution in a cylindrical specimen during its rapid resistive self-heating. Possible future directions for this program include the development of new methods for measuring the thermophysical properties of advanced aerospace alloys in both the solid and liquid phases.

The principal objective of the current research on pressure metrology near and above atmospheric pressure is to understand and quantify the effects of using different gases and different modes of operation (i.e., absolute mode versus gage mode) on the measurement of pressure with gas-operated piston gages. The emphasis of the work to date has been on the development of two new apparatus. One apparatus will make it possible to use two piston gages to study a third with different gases and with modes of operation that vary continuously from absolute mode to gage mode; the other will provide detailed information on the forces exerted on an oscillating piston by the gas in the narrow annulus between the piston and the cylinder. The Division has established excellent relations with the major U.S. manufacturers and users of pressure gages. Examples include a leadership role in the development of recommended practices for the calibration and use of piston gages, and the initiation of a new Cooperative Research and Development Agreement with one of the manufacturers to characterize newly designed large-diameter (50 mm) piston gages made of an advanced material that can be machined to extremely close tolerances (500 nm). This project has the potential to lead to a new type of primary pressure standard in the important range near atmospheric pressure.

There were several significant advances during the past year in the area of pressure measurements near and below atmospheric pressure. The first was the completion of a new orifice-flow primary pressure standard that fills a gap in NIST's primary pressure standards

where many important industrial processes operate, including sputtering and plasma processing of semiconductors, freeze drying of food, and superalloy casting. The new standard is capable of rapid and flexible operation in calibration services over the range from 10^{-4} to 10^{+2} Pa and overlaps NIST's primary standards at both higher and lower pressures. Called the Transition Range Standard, the new system is also ideal for studying a variety of flow phenomena in the range between molecular and viscous flow. A second noteworthy accomplishment was the completion of a new water-flow standard that allows the generation of water vapor at pressures from below 10^{-7} Pa to almost 10^{-1} Pa. Water is a ubiquitous contaminant in vacuum systems, and quantitative measurements are crucial in the processing of semiconductor materials and in the outgassing of satellite components in space systems. This program is part of a longer-term effort to develop measurement methods and standards to calibrate vacuum and process instrumentation for use with other active gases such as hydrogen, oxygen, and carbon monoxide, and ultimately, with process gases. A growing part of this effort is the use of non-intrusive, species-specific optical techniques such as infrared absorption, multiphoton ionization, and laser-induced fluorescence to perform quantitative measurements on low-density gases and gaseous mixtures.

FY92 was an excellent year from the point of view of recognition. Dr. J.M.H. (Anneke) Levelt Sengers received the rare distinction of being elected a Member of the National Academy of Engineering for her work on the critical behavior and thermophysical properties of industrially important fluids and fluid mixtures. In addition, Dr. Levelt Sengers and her husband, Dr. Jan V. Sengers, received honorary doctorates from the Technical University of Delft, The Netherlands for their outstanding research and leadership in the area of thermophysics. Dr. Howard J.M. Hanley received a Humboldt Research Award for Senior U.S. Scientists for his seminal work on the behavior of fluids out of equilibrium. Dr. Ared Cezairliyan received an Outstanding Mechanical Engineer Award from Purdue University for his pioneering work on ultrafast measurements on solids at high temperatures. Dr. Charles D. Ehrlich received the Department of Commerce Bronze Medal for his outstanding contributions to the establishment of the Nation's first leak-rate measurement standards and calibration services. Drs. Graham Morrison and Mark O. McLinden received the NIST Applied Research Award for their development of extremely accurate and practical models for predicting the properties of alternative refrigerants and refrigerant mixtures. Dr. Morrison and Dr. Marcia L. Huber received NIST Measurement Service Awards for their outstanding contributions to the NIST Standard Reference Data Program, and Dr. J.P. (Pat) Looney received an NIST Measurement Service Award for his extraordinary efforts to provide high-quality vacuum calibration services.

The Division continues to be organized into five groups: Properties of Fluids (Boulder, CO), Fluid Science, Subsecond Thermophysics, Pressure, and Vacuum. The following Technical Reports describe the activities and major accomplishments of these groups in more detail.

**B. Selected Technical Reports
(Thermophysics Division)**

1. Calibration and Test Services Performed by the Thermophysics Division

S.W. Doty, R.G. Driver, C.D. Ehrlich, A.R. Filippelli, R.W. Hyland, J.P. Looney, W. Markus, C.R. Tilford, S.A. Tison, D.B. Ward, and B.E. Welch

The Thermophysics Division provides calibration and special test services to both the domestic and international communities in the areas of pressure, vacuum, and leak rate. Pressure and vacuum calibrations span sixteen orders of magnitude, from 10^{-7} Pa to almost 10^9 Pa, and leak-rate calibrations now cover 10^{-14} mol/s to 10^{-6} mol/s. The Division develops and maintains a wide variety of primary and secondary standards in support of these services.

Calibration income to the Division totalled \$300K in FY92. This was derived from the calibration of 65 piston gages, 27 low-pressure gages, 13 ionization gages, 20 spinning rotor gages, and 18 leaks. This level of work has remained fairly constant ($\pm 10\%$) over the last four years, despite increases in the calibration surcharge passed on to the customers during this period. Delivery of vacuum calibrations was slowed during FY92 and work was not solicited because of the loss of a key staff member. The customer base for the leak calibrations has shifted somewhat away from the aerospace industry and more towards the automotive industry. Vacuum and low-pressure-gage calibration customers are still predominantly from the aerospace, defense, utility, and process (semiconductor, pharmaceutical) industries. The piston-gage calibration customers are distributed primarily among the military, other government laboratories, utility companies, gage manufacturers, and private industry.

Several significant advances have been incorporated in the calibration services this year. A new capability for calibrating high-pressure (100 MPa) gas-operated piston gages has been developed, and the first customer gage that utilizes the new gas-operated, oil-lubricated technology has been calibrated. A new standard that operates in the "transition" range of pressures (10^{-2} to 10^2 Pa) has been developed to fill a long-existing gap in our vacuum calibration capabilities (see Report #2). This pressure region is of great importance in the industrial sector, especially the semiconductor industry, and an increased calibration workload is anticipated in FY93. The leak service has been expanded over a broader range of leak rate, and capillary leaks that operate with a variety of gases, including refrigerants, are now being accepted for calibration.

2. Performance of the New Transition Range Primary Vacuum Standard

**J.P. Looney, J. Setina (Institute of Electronic and Vacuum Technology, Slovenia),
R.W. Hyland, and C.R. Tilford**

Many important industrial processes, including freeze drying, sputtering, and chemical vapor deposition, occur in a low-pressure environment (0.1 to 100 Pa), and in many cases accurate control of the process pressure is critical to product yield and quality. However, this "transition range" of pressures where the mean free path in the gas is comparable to typical system dimensions is a particularly difficult one in which to develop vacuum standards, and these difficulties have resulted in a gap in the NIST primary standards. Over the past two years, we have closed this gap with the development of a vacuum standard designed to operate over the range 0.001 to 100 Pa, which covers not only the transition range, but overlaps with existing primary standards at both higher and lower pressures. Our primary low-pressure standards, based on ultrasonic interferometer manometers (UIMs), operate over the pressure range 1 Pa to 320 kPa; our high-vacuum standards operate over the range 10^{-7} to 0.1 Pa. Comparisons of the new transition range standard with both the higher- and lower-pressure standards have demonstrated good agreement. The new standard has already been used for (a) the calibration of 25 customer gages, (b) an investigation of the accuracy of the spinning rotor gage (SRG) viscosity correction (see Report #5), and (c) experiments to characterize the conductances of orifices and tubes in the transition range (see Report #6).

The transition range standard is based on the orifice-flow technique used in existing NIST high- and ultrahigh-vacuum standards. The extension to higher pressures is accomplished by using a series of three conductances that maintain ideal molecular flow to successively higher pressures. These conductances are an 11-mm-diameter orifice for use at the lower pressures, a 2.2-mm-diameter orifice for use at the intermediate pressures, and a micro channel plate (an array of 3 million 5-micrometer-diameter holes) for use at the higher pressures.

The transition range standard has been compared with the primary ultra-high vacuum standard and agreement for pressures up to 0.01 Pa was found to be better than 0.5%, which is less than the combined uncertainties of the two standards. Between 1 and 25 Pa, the transition range standard agrees with the low-range UIM to within 0.1%, which is significantly less than our uncertainty estimate for the transition range standard in this range. Gages are now being accepted for calibration over the entire pressure range on a special test basis.

3. An Absolute Standard Source for Low-Density Water Vapor

D.F. Martin, C.R. Tilford, and S.A. Tison

Water vapor is the most common residual gas in vacuum systems and generally one of the most unwelcome. Part-per-million or smaller quantities of water can destroy the adherence of optical coatings and cause major changes in semiconducting and microcircuit interconnect materials. Water outgassed from satellite components can freeze onto cooled optics and detectors and has caused the loss of several very expensive infrared and ultraviolet space-borne telescopes. These problems have generated a demand for ever-lower levels of water partial pressures. In the case of semiconductor processing, this task is complicated by the recognition that the limiting factor often is water generated in the process chamber, while at the same time there is a demand for shorter pumpdown and clean-up times to optimize the use of increasingly expensive capital equipment. Evaluation and solution of these problems require accurate measurements of water partial pressures in the high and ultrahigh vacuum ranges. However, standards for water pressures have been very limited and are generally developed for specific research problems. Moreover, very little is known about the effects of water vapor on vacuum instruments, and the capability to calibrate with water over any significant range does not exist.

To begin to address these problems, we have developed a prototype Knudsen-effusion water source and used it with our orifice-flow standards to generate water vapor pressures from 2×10^{-5} to 3×10^{-2} Pa with uncertainties of about 3%. The prototype water source consists of pure, degassed liquid water separated from the orifice flow standard by a 25-micrometer-thick stainless-steel foil with an array of 3- to 5-micrometer-diameter laser-drilled holes. This prototype standard has been used to obtain preliminary data on the water sensitivities of several different vacuum gages and partial pressure analyzers, and to examine the effect of water operation on the sensitivities for other gases. Among other things, it has been found that the operation of vacuum instruments can perturb the water vapor pressures by several percent. Encouraged by the success of the prototype system, we have constructed a new water-flow standard of the same design but with an extended range from below 10^{-7} Pa to almost 10^{-1} Pa. The new standard should be in service by the end of 1992.

4. Optical Measurements of Low Gas Densities

J.P. Looney

In a wide variety of applications, the measurement and control of "reactive" contaminant gases such as H_2O , CO , and O_2 are critical to product yield and/or lifetime. However, traditional vacuum standards and measurement techniques are not compatible with gases that strongly adsorb or chemically react at the surface of the hot cathodes used in the ion sources of mass spectrometers and hot-cathode ionization gages. A potential solution to this problem

is the use of spectroscopic measurements, provided they have the sensitivity to generate quantitative signals at low gas densities. Many spectroscopic techniques have been developed for diagnostics in chemically reactive systems, but generally for applications at moderate pressures (1 to 1000 Pa). The applicability of spectroscopic techniques to gas density measurements in high-vacuum environments has not been firmly established.

During the past two years, the Division has undertaken a series of exploratory experiments on optical techniques for low gas density measurements in collaboration with the Electron and Optical Physics Division (PL), the Molecular Physics Division (PL), and the Fire Measurement and Research Division (BFRL). During this past year, experiments were conducted using resonance-enhanced multi-photon ionization coupled with time-of-flight mass spectrometry (REMPI-TOFMS) for low gas density measurements of Xe, O₂, N₂, and CO. As would be expected for such a highly nonlinear spectroscopy, the results of these experiments show that ultimate detection limits are highly species and optical-transition dependent, and dependent on laser parameters such as focusing, beam alignment, and pulse energy. Nonetheless, with proper control of the laser parameters, ultimate detection limits on the order of 10⁴ molecules/cm³ (10⁻¹⁰ Pa) were demonstrated for CO (an exceptionally favorable case), while detection limits on the order of 10⁷ to 10⁶ molecules/cm³ (10⁻⁷ to 10⁻⁸ Pa) were demonstrated for more typical molecular transitions in N₂ and O₂. After a suitable normalization for laser pulse energy variations, it is possible to make quantitative measurements with an uncertainty of about 15%, and we believe this can be improved further by normalizing on an individual laser shot basis. Finally, it was found that REMPI-TOFMS has exceptional common-mode rejection; that is, signals from species A are not perturbed or influenced by the presence of species B. For example, we found that the signal from the low-level background of 10⁶ molecules/cm³ (10⁻⁸ Pa) of CO present in an ultrahigh vacuum chamber was not affected, to within 15%, by N₂ pressures as much as five orders of magnitude higher. Since N₂ and CO are separated by only 0.001 atomic mass units, this is a classic test for mass spectrometers; most commercial mass spectrometers of the quadrupole type cannot approach this level of performance.

5. Developments in Vacuum Instrumentation

R.W. Hyland, F.P. Long, J.P. Looney, J. Setina (Institute of Electronic and Vacuum Technology, Slovenia), C.R. Tilford, and S.A. Tison

Since vacuum standards have become available only recently, and reliable characterization of instrumentation was not possible previously, vacuum instrument characterization has been a significant part of the NIST vacuum standards program. This past year we have moved beyond characterization to the development of improvements to remedy previously identified problems.

First, we have undertaken the development of an improved spinning rotor gage (SRG). The SRG is a molecular drag gage that determines pressures by measuring the rate of slowing of a rotating magnetically-suspended steel ball due to collisions with the ambient gas. The SRG has superior stability (1-2% over a few years time) and is now widely used as a transfer standard between 10^{-4} and 10^{-1} Pa. However, there are several limitations. One of these is the questionable accuracy of a viscosity correction that is incorporated in the instrument and that allows operation to the higher pressures used widely in processing industries (up to 100 Pa). Using our new transition range standard (see Report #2), we have checked the high-pressure performance of several samples of the two different commercial SRGs and found errors in the indicated pressure as large as a factor of two. However, we have been able to develop an algorithm that is accurate to within 1% for different gases and gage configurations. A second and more extensive project has been the development of a new personal-computer-based electronic control unit. The commercial SRG control units are poorly-documented microprocessor-controlled black boxes. They do not allow user control of important operating parameters, and they limit the operating range at lower pressures. Our new control unit allows user control of all operating functions, performs all data acquisition and reduction using well documented algorithms, allows arbitrarily long measurement times (permitting operation to lower pressures), and allows the operation of multiple units from a single personal computer, all at a reduced cost. A prototype unit has been operated successfully, several modified units are being produced for our internal use, and commercial licensing agreements are being discussed.

A second gage of considerable importance for both metrology and process control between 0.1 and 1000 Pa is the capacitance diaphragm gage (CDG). Our evaluations of CDG performance over the years have found them to be limited by temperature-change-induced zero instabilities, abrupt shifts in sensitivity, and thermal transpiration nonlinearities. We have initiated a program to try to improve the performance of these devices. Initial results indicate that improved temperature control can significantly improve zero stability, and control at room temperature, using thermoelectric modules, will linearize the output in the transition pressure range. We will continue to examine alternative construction techniques and materials aimed at minimizing the sensitivity shifts.

Partial pressure measurements are yet another major direction for our work, and we have undertaken to determine the characteristics and limits of partial pressure analyzers (PPAs). This work continued this past year with a focus on the effects of exposure to reactive gases, particularly water and oxygen.

6. Characterization and Modeling of Transition-Range Flow Elements

J.P. Looney, R.D. Mountain, and S.A. Tison

The accurate generation and understanding of a wide range of flows is important for the vacuum processing and equipment industries. In particular, transition flow is important in the design of molecular drag vacuum pumps, modeling and control of plasma and chemical vapor deposition semiconductor processing, vacuum gage calibration, and vacuum gage and system design. While theories for the extremes of molecular flow and viscous flow are well established, the theory for the transition from molecular to viscous flow is not: even for simple geometries and low gas densities, tractable models are far too simplistic. Several empirical models exist for transition flow, but their validity is not well established either, particularly for large pressure gradients along the conductance elements.

To understand the physical processes that govern transition flow, we have undertaken an experimental investigation of the flow through tubular elements. Tubular elements were chosen for three reasons: their common use as leaks to admit gas into vacuum systems, the existence of empirical models describing their behavior for small pressure differentials, and their suitability for further theoretical modeling.

Some empirical models and references in the literature claim that for small pressure differences the conductance of a tube will have a minimum in the transition region between molecular and viscous flow; other models do not predict such a minimum. We have verified experimentally the existence of this minimum over a wide range of pressure gradients for cylindrical tubes with diameters ranging from a few micrometers to 2 mm. For tubes with large pressure gradients, the minimum is about 20% below the conductance in the molecular limit. Data are currently being obtained to develop an empirical model for flow through tubes that will be valid for all flow regimes and pressure gradients.

To complement the experimental and theoretical work, we are using Monte-Carlo techniques to predict the conductances of both tubes and orifices in the molecular and transition flow regimes. To date, results have been obtained for orifices and short tubes in the molecular and near-molecular regimes. These results are in quantitative agreement with our experimental data and existing analytical kinetic-theory calculations.

7. Non-Classical Effects in Gas-Operated Piston Gages

R.G. Driver, C.D. Ehrlich, J.C. Houck (Guest Researcher), J.L. Kelley, T.R. Lettieri, B.A. Ratnam, J.W. Schmidt, and B.E. Welch

Gas-operated deadweight piston gages are the instruments of choice in the atmospheric pressure range for most applications where high accuracy, low cost, ease of use, and transportability are important considerations in the transfer of the unit of pressure between laboratories or from the laboratory to the field. The increasing use of 'accuracy ratios' as regulatory guidelines in propagating uncertainties in effective area has led to requests for total uncertainties at the national standards level of well under 50 parts per million. These levels of uncertainty tax the performance of some of the best available instruments. In particular, the effective areas of these instruments are found to depend on the gas being used, and on whether or not the gage is operating in the absolute mode (essentially vacuum above the piston) or the gage mode (atmospheric pressure above the piston), at the tens of parts per million level. Such effects were not anticipated to be so large and are still ignored by many.

To investigate these gas and mode-of-operation effects, the Division has developed two new apparatus: the Three-Piston-Gage Apparatus, which utilizes two piston gages to carefully characterize a third, and the Dynamic-Piston-Gage Apparatus, which probes the decay of small amplitude oscillations of the piston to understand the forces acting in the annular region between the piston and the cylinder. Work this year with the three-piston-gage apparatus has concentrated on automating the floating of all three pistons simultaneously to reduce the noise level that exists when floating the pistons manually. Preliminary data have been obtained in this configuration for two gases in both modes of operation. At the present time, the uncertainties associated with the apparatus permit a bound of ± 10 parts per million to be placed on the gage-to-absolute-mode effect for the particular atmospheric-pressure-range gage under investigation. Additional techniques such as interchanging the masses will be used in the future to further reduce the uncertainties. The dynamic-piston-gage apparatus also has undergone significant improvement in its design and function this year. The volume under the piston has been made variable and reconfigured to reduce thermal losses. Electromagnets initiate piston oscillations, and a centered inductive displacement sensor eliminates rotational noise. These and other improvements have allowed measurements of the natural oscillation frequency to one part in 10^4 and measurements of the quality factor to one part in 10^3 . These results are improvements by factors of 70 and 10, respectively, over the initial design.

8. Development of a High-Pressure Gas-Operated Piston Gage Calibration Service

S.W. Doty and C.D. Ehrlich

Recent advances in commercial gas-operated piston gage technology have brought to the market two different types of gages that operate to high pressures (up to 110 MPa). Customer interest in NIST traceability for this gas pressure range prompted the Division to develop a prototype laboratory system capable of providing such a calibration at an acceptable level of uncertainty (less than 100 parts per million in effective area). The system uses a NIST oil gage as the standard, with a directly visible gas-liquid interface and a liquid-liquid differential pressure (DP) cell connecting the standard and test instruments. Traditional cross-float techniques are used.

While the system as it exists can be used for calibrations, there are difficulties with this arrangement, including the dissolution of gas in the liquid (oil), the lack of constancy of the oil level, and the removal of trapped bubbles in the DP cell. Although good sensitivity was usually maintained, the presence of bubbles undoubtedly contributed to the overall random noise in the system, which was at the level of 20 parts per million. To reduce uncertainties further, it will be necessary to develop alternative system configurations, such as the use of a DP cell as the gas-liquid separator, or the removal of the DP cell while maintaining the gas-liquid interface.

The designs of the two commercially available high-pressure gas gages differ in that oil fills the gap between the piston and cylinder in one of the instruments but not the other. For applications where the presence of oil is undesirable or even hazardous, it will be necessary to develop a technique in which the oil can be eliminated completely from the calibration process. Possible techniques include the use of a DP cell with a gas-operated standard gage, or the removal of the DP cell entirely, with direct gas-gas communication between two gas-operated piston gages. A NIST-owned gas piston gage standard will be developed for this purpose.

Due to the problems of using oil to calibrate a high-pressure gas piston gage, efforts are underway to investigate the alternative methods mentioned above. The best technique will be used to establish a NIST calibration service for high-pressure gas piston gages.

9. Release of New Version of REFPROP

**J.S. Gallagher, M.L. Huber, M.O. McLinden, M.R. Moldover, and
G. Morrison**

REFPROP is a package of user-friendly personal-computer programs that incorporates a database developed in the Thermophysics Division. The package is used by engineers to screen a wide range of environmentally-acceptable refrigerants as possible replacements for currently-used refrigerants. The tables of thermophysical properties produced by REFPROP are used to predict the efficiency and capacity of machinery that will employ alternative refrigerants. In contrast with most properties packages, the source code for REFPROP is part of the package, and some users have incorporated it into proprietary models for specific types of machines.

During FY92, REFPROP 3.0 was released. REFPROP 3.0 provides tables for 26 pure refrigerants and their mixtures with as many as 5 components. The thermal conductivity and viscosity are provided with the thermodynamic properties.

REFPROP 3.0 contains a highly accurate modified Benedict-Webb-Rubin (MBWR) equation of state for R134a that correlates the most recent thermodynamic information for this leading candidate replacement refrigerant (see Report #10). This MBWR equation also serves as the reference function for an extended-corresponding-states model for the thermodynamic properties of all 26 pure fluids on the REFPROP menu and for the transport properties of these fluids and their mixtures. A simpler corresponding-states model is used to estimate the surface tension of the pure refrigerants; surface tension is used to correlate boiling heat transfer.

The Carnahan-Starling-DeSantis (CSD) model is available for all 26 fluids and is used for all calculations of the thermodynamic properties of mixtures. An explicit rule for predicting mixing parameters from dipole moments is incorporated in REFPROP 3.0. The rule is applicable to all but one of the fluids on the menu.

Over 200 copies of REFPROP have been sold by the NIST Standard Reference Data Program. The program has been adopted as a standard by the air conditioning and refrigeration industry.

In addition to releasing Version 3.0 of REFPROP, during FY92 we developed new MBWR equations of state for R123, R124, and R270 and will add them to the next version of REFPROP. As described in Report #13, we also developed a new model that explicitly incorporates dipole moments in a CSD-type equation of state. The new model is superior to the CSD model for polar fluids such as R32 and its mixtures and will be incorporated into REFPROP when R32 is added. Research is continuing to incorporate ammonia, water, and

their mixtures into the package. Ultimately, we expect REFPROP to include all stable, small molecules that could plausibly be used as working fluids in thermal machinery.

10. Standard Reference Equations of State for Alternative Refrigerants

M.L. Huber, M.O. McLinden, B.A. Younglove, and D.G. Friend

The Division has developed high-accuracy, standard-reference-quality equations of state for refrigerants 134a, 123, and 124—three of the most promising replacements for the fully halogenated chlorofluorocarbon refrigerants. The fitting of these equations has been coordinated with the experimental work of the Division (see Report #11) and our international activities (see Report #14). In fitting the equation of state, we have employed a multivariable fitting technique that allows us to fit simultaneously all of the available experimental data, including “higher order” data such as sound speed and heat capacity. We also have adapted this technique to a personal computer and have added on-screen graphical displays of the goodness of fit; this capability permits us to explore many more possibilities for weighting the data to arrive at the best possible representation of the properties of the fluid given the form of the equation of state.

For refrigerants, we have used the same modified Benedict-Webb-Rubin (MBWR) equation of state that has proven so successful in modeling the properties of hydrocarbons, cryogenic fluids, and simple inorganic molecules. Programming effort is minimized by using a common form for the equation of state, and new fluids can be incorporated readily into our existing properties packages. The MBWR equation for R134a serves as the reference fluid formulation for the extended-corresponding-states portion of the REFPROP computer package distributed by the NIST Standard Reference Data Program. The equations for R123 and R124 will be incorporated into the next revision of REFPROP. In the coming year, we will be developing similar equations for several additional new refrigerants, including R125 and R32. We also are exploring different functional forms for the equation of state in our continuing effort to improve the accuracy and range of applicability of the thermodynamic formulations.

11. Measurements of the Equilibrium Properties of Alternative Refrigerants

D.R. Defibaugh, D.E. Diller, K.A. Gillis, A.R.H. Goodwin, J.B. Howley, J.W. Magee, G. Morrison, M.R. Moldover, R.A. Perkins, J.W. Schmidt, L.J. Van Poolen (Calvin College), and L.A. Weber

The Thermophysics Division has been involved in measuring the thermodynamic properties of candidate refrigerants since 1982. Initially, this effort was coordinated with the Building Environment Division's (BFRL) program to develop more efficient heat pumps and cooling

systems. With the advent of the Montreal Protocol restricting the future production of fully-halogenated chlorofluorocarbon refrigerants, the need for a wide variety of environmentally-acceptable substitutes became obvious. In response to the Montreal Protocol, and with advice from other government agencies and industry, the Division developed a priority list of candidate replacements and a strategy for determining their thermophysical properties. The strategy included developing new apparatus for characterizing samples and for acquiring data efficiently. For the leading candidate replacements, we scheduled very accurate, wide-ranging measurements. Less comprehensive measurements, suitable for screening purposes, were scheduled for a second tier of candidates and for "long shots." As the program has progressed, the emphasis on characterizing mixtures has grown. We also have developed an approach to disseminating the results of the measurements in a form that is most useful to the industry. We correlate the data ourselves and distribute the results via REFPROP, a user-friendly computer package (see Report #9).

During the past year, extensive additional measurements were made. For brevity, they are listed by type of data and refrigerant, with mixtures of refrigerants A and B indicated by A+B:

1. Gas-phase PVT (Burnett Apparatus): R32, R124, R125.
2. Liquid-phase PVT: R32, R123, R124, R125.
3. Coexisting densities: R22, R32, R124, R134a, R152a, R143.
4. Constant volume heat capacity (liquid phase): R32, R125.
5. Vapor pressure: R32, R142b.
6. Critical parameters: R32.
7. Vapor-phase speed of sound: R124, R125.
8. Phase equilibria: R32+R125, R134a+R152a.

Portions of this work were sponsored by EPRI, EPA, DoE, and the air conditioning and refrigeration industry.

An important part of our research program on alternative refrigerants is the development of applicable tools for chemical analysis and characterization; this is especially important for refrigerants in that many of them are difficult to acquire in large quantities and/or pure form. These tools include the design and modification of analytical instrumentation and sensors, the development of analytical methods, and the generation of standard data to support chemical analysis. In the area of analytical instruments, we recently designed a new low-temperature cell for infrared spectrophotometry, for which a U.S. patent is pending. We also designed a device for sample pre-concentration, for which a U.S. patent has been granted. These developments in hardware follow the advances made in recent years in chromatographic injectors for refrigerants. In the areas of analytical methods and data, we have developed a chemical analysis protocol to support the thermophysical property measurement program. This protocol includes tests for organic and inorganic impurities, heavy contaminants, and chemical reaction screening. The protocol is supported by a data base of analytical

information on alternative refrigerants and their possible reaction/decomposition products. Included for each fluid are our own measurements of mass spectra, infrared spectra, ^1H , ^{13}C , and ^{19}F nuclear magnetic resonance spectra, ultraviolet-visible absorption spectra, chromatographic specific retention volumes, and partition coefficients.

12. Transport Properties of Alternative Refrigerants

R.A. Perkins, D.E. Diller, D.C. Ripple, D.G. Friend, M.L. Huber, A. Laesecke (Guest Researcher), O. Matar (Imperial College, England), S. Matthes (Technical University, Germany), and C.A. Nieto de Castro (Instituto Superior Tecnico, Portugal)

The measurement and correlation of transport properties for alternative refrigerants is complementary to the study of their equilibrium properties. The viscosity and thermal conductivity are required to determine the size of refrigeration equipment and the efficiency of foam insulation layers using new alternative refrigerants. The Thermophysics Division has strong programs to measure, correlate, and predict the thermal conductivity and viscosity of proposed replacements for chlorofluorocarbons. Pure fluids have been the focus of the program this year, but work in the coming year will include refrigerant mixtures.

The Thermophysics Division has the capability to study the thermal conductivity and viscosity of these new alternative refrigerants over an extremely wide range of temperature and pressure using a variety of measurement techniques. Two transient hot-wire thermal conductivity instruments are available which cover the temperature range from 60 to 750 K at pressures to 70 MPa. For measurements of polar refrigerants, these instruments can operate either with bare platinum hot wires using a polarization technique or with an electrically insulated tantalum hot-wire cell. Two torsionally oscillating quartz-crystal viscometers are available which cover the temperature range from 60 to 600 K at pressures to 70 MPa. A capillary viscometer is also available which covers the temperature range from 250 to 330 K at pressures to 1 MPa. An accurate vibrating wire viscometer also is being developed for use over a wide range of temperature and pressure.

The correlation and prediction of the transport properties of alternative refrigerants is our final output product. Using data measured in the Thermophysics Division and obtained from the literature, we have developed correlations for specific fluids, incorporating theory where possible. In the case of thermal conductivity, we have observed a very significant critical enhancement that can be modeled quite well with mode-coupling crossover theory. Extended-corresponding-states approaches also are being developed to correlate measured transport properties and to predict the transport properties for proposed alternative refrigerants, including mixtures, when no data are available.

During the past year, comprehensive measurements of the thermal conductivity and viscosity of R32, R123, R124, R125, and R141b have been made in their liquid, vapor, and supercritical fluid phases. Vapor-phase thermal-conductivity measurements have been made from 280 to 330 K on R143, R227ea, R236ea, and R245ca. Saturated liquid viscosity measurements have been made from 250 to 310 K on R134a, E134, and E245, and on equimolar mixtures of R125+R134a, R32+R134a, and R32+R124. The Division received support for this work from the air conditioning and refrigeration industry, DoE, and EPA.

13. New Model for Refrigerant Mixtures Based on Dipole Moments

G. Morrison

The Carnahan-Starling-DeSantis (CSD) model is used widely to represent the equation of state of refrigerant mixtures. The CSD model mimics the repulsive part of the intermolecular potential with a temperature-dependent hard-sphere diameter, and it also includes a temperature-dependent attractive term. Under the operating conditions of refrigerators (0.05 to 2 MPa), this model can represent the vapor pressure and the densities of the liquid and vapor phases of many refrigerants and their mixtures within 0.1%. These properties, together with the ideal-gas heat capacity, are the key ones for estimating the efficiency and capacity of thermal machinery. However, the CSD equation of state does not fit the properties of highly polar fluids nearly as well as it fits the properties of fluids with either small or zero dipole moment.

To address this problem, the CSD model has been improved by adding a term that explicitly accounts for dipole moments. The added term is a modification of Stell's representation of the hard-sphere fluid with embedded dipoles. With the additional term, the model has become known as the Carnahan-Starling-DeSantis-Morrison (CSDM) model. Both the free energy and equation of state for the CSDM model reduce to the corresponding CSD expressions in the limit of zero dipole moment.

Initially, we have used the CSDM expressions to represent data for R32, R125, R134a, and R152a. These fluids were chosen because they are all highly polar and because the refrigeration industry believes that their mixtures might serve as substitutes for R22. For these pure polar fluids, the CSDM model is somewhat better than the CSD model. We also have acquired data for the mixtures R32+R134a, R32+R152a, and R134a+R152a. For these mixtures, the CSDM model is vastly superior to the CSD model. Data now are being acquired for mixtures of polar fluids (such as R32) and non-polar fluids (such as propane, butane, and cyclopropane). These data will be used to test the CSDM model for this key situation. Additional terms to account for non-sphericity and polarizability will be added to the CSDM model in the future.

The form of the dipolar term in the free energy is based on perturbation theory, and it overestimates the dipolar contribution when the reduced dipole moment approaches unity. This occurs for very polar fluids at low reduced temperatures. Thus, it is not surprising that the present version of the CSDM model is unsatisfactory for ammonia, water, and their mixtures under conditions encountered in thermal machinery. Further research will be required to represent these important fluids with a CSDM-style model.

14. International Activities on CFC Alternatives

M.O. McLinden, W.M. Haynes, and R.A. Perkins

The Thermophysics Division initiated and serves as "operating agent" (coordinator) for a project entitled "Thermophysical Properties of the Environmentally Acceptable Refrigerants", under the auspices of the International Energy Agency (IEA). The objectives of this project, known as Annex 18, are (a) to provide a forum for the exchange of information and data and for the coordination of activities on the thermophysical properties of environmentally acceptable refrigerants and (b) to determine (via experimental measurements and the evaluation and correlation of data) the thermophysical properties of these fluids leading to the publication of a comprehensive, internationally-accepted properties bulletin. Annex 18 was approved formally by the IEA in early 1990. At present, Austria, Canada, Germany, Japan, Norway, Sweden, the United Kingdom, and the United States are members of the Annex. In addition to NIST, the United States is represented by Texas A&M University, the University of Idaho, and Cornell University. Meetings of the Annex have been held in Japan, Germany, and the United States.

The focus of Annex efforts in FY92 was an evaluation of experimental data and equations of state for refrigerants 134a and 123. This is the crucial step for the Annex to select the best equation of state for the properties of these two leading alternatives to the fully halogenated chlorofluorocarbon (CFC) refrigerants; this equation will then form the basis for a properties bulletin that is expected to become the de facto international standard. The University of Idaho and Imperial College were assisted by NIST and Keio University, Japan in this task. Work also continued on the compilation of thermophysical property data for more than a dozen other alternative refrigerants. The process of updating the very successful survey of current research on the measurement and modeling of refrigerant thermophysical properties also was begun. As with the first survey (published in 1991 as NIST Internal Report 3639), NIST will coordinate the survey and will be assisted by Keio University, Japan and the National Engineering Laboratory, United Kingdom; Texas A&M University will compile the survey responses and prepare the final report. In the coming year, the original three-year term of the Annex will almost certainly be renewed. The focus of future work will shift to replacements for R22 and other hydrochlorofluorocarbon (HCFC) refrigerants.

The Division also participated in the second technical reassessment associated with the Montreal Protocol on Substances that Deplete the Ozone Layer, the international treaty that regulates the production of CFCs and HCFCs. This review was coordinated by the United Nations Environment Programme. M.O. McLinden served on the panel responsible for the "Technical Options Report" on refrigeration and air-conditioning uses of CFCs and HCFCs and as lead author for the "Refrigerant Data" section of the report. This report serves as input for the re-negotiation of the phase-out timetable and other provisions of the Protocol.

The Division has worked very actively with ASHRAE. (Although based in the U.S., ASHRAE is an international organization that "leads the way" for the entire refrigeration industry.) M.O. McLinden coordinated the update of the tables and charts of refrigerant properties in the ASHRAE Handbook of Fundamentals—a reference volume that is distributed to over 50,000 practicing engineers worldwide; the update includes six new alternative refrigerants. Dr. McLinden also serves on the ASHRAE committee responsible for classifying the alternative refrigerants; classification is required by many building codes before a new refrigerant can be used in commercial and residential systems.

Finally, the Division participated in IUPAC activities on the thermal conductivity of alternative refrigerants. Highly polar refrigerants present special difficulties for some of the standard techniques for measuring thermal conductivity. At the meeting of the IUPAC Transport Properties Subcommittee in Rostock, Germany, R.A. Perkins presented techniques developed at NIST for dealing with the problems presented by the alternative refrigerants and participated in discussions to set up an international round-robin test series on a "standard" refrigerant for quality control purposes.

15. Advances in the Theory and Modeling of Thermophysical Properties

J.C. Rainwater, D.G. Friend, M.L. Huber, H.J.M. Hanley, B.A. Younglove, M.O. McLinden, R.T. Jacobsen (Univ. of Idaho), C.D. Holcomb, and L.J. Van Poolen (Calvin College)

A primary focus of the Division's theoretical effort is to develop and apply microscopic theories of fluids to the prediction and correlation of both equilibrium and nonequilibrium behavior of pure fluids and mixtures. The modeling efforts encompass broad ranges of state variables and incorporate theoretical advances as appropriate. Correlations of fluid properties and predictive models are distributed through the Standard Reference Data Program of NIST in the form of computer packages developed in the Division.

During the past year, we have worked with a quantum generalization of the Boltzmann equation to develop an analog of our classical approach to the density dependence of the viscosity of gases. This work allows our successful theory for transport properties to be extended to systems such as helium and hydrogen whose thermal wavelength is large

compared to the interparticle spacing, and it puts the theory in a more fundamental context. A mode coupling approach to the critical enhancement of the thermal conductivity was applied to the alternative refrigerant R134a, and corresponding-states arguments based on this approach are being developed.

The modified Leung-Griffiths model was used to develop an accurate model for the surface tension of air. This model will form part of the standard package for the thermophysical properties of air prepared for the National Aerospace Plane Project. An extension of the Clausius-Clapeyron equation was used with the modified Leung-Griffiths model to calculate enthalpy and entropy differences across mixture dew-bubble phase boundaries. We developed computer code to implement the theory numerically and obtained good agreement with independent calculations for CO₂+propylene and with experimental data for pentane+benzene.

Finally, the development of highly accurate correlations of the thermophysical properties of pure fluids has continued. Projects on alternative refrigerants, including R134a, R123, and R124 are essentially complete. Projects on the intermediate alkane systems, heptane and isohexane, are being pursued. Although many of the thermodynamic surfaces developed in the Division are based on the modified Benedict-Webb-Rubin equation, alternative equations are being developed. A novel method based on simulated annealing to optimize the terms of a correlating equation is being developed and has been tested on vapor pressure data. We will extend this technique to the entire thermodynamic surface in the coming year.

16. Release of New Version of MIPROPS

D.G. Friend, M.L. Huber, J.C. Rainwater, and B. McGarvey (Ranum High School, Westminster, CO)

The NIST Thermophysical Properties of Pure Fluids Database (also called NIST Standard Reference Database 12 and formerly called MIPROPS) is a primary mechanism for the dissemination of evaluated pure fluid thermophysical properties. These standard reference data are the result of an extensive body of research, critical evaluation, and correlation within the Division and are used in problems of custody transfer, process design, and process simulation in the aerospace, chemical, and energy-related industries. A variety of trade groups and technical organizations have adopted these computer programs as working standards.

Version 3.0 of the database, which was released during FY92, provides great flexibility in the choice of input properties, output properties, and units in a user-friendly personal computer package. Properties at the desired state points, or tabular information in the form of isochores, isobars, isotherms, isentropes, etc., may be displayed and saved in a file for further use. Five new fluids have been added to the database. The fluids now available are

argon, isobutane, normal butane, carbon dioxide, carbon monoxide, deuterium, ethane, ethylene, helium (including superfluid states), normal hydrogen, para-hydrogen, methane, nitrogen, nitrogen trifluoride, oxygen, propane, and xenon. For each of the supported fluids, the equilibrium thermodynamic properties are based on a multiparameter equation of state that gives accuracies in density of the order of 0.1%. For most of the fluids, transport properties (viscosity and thermal conductivity), with accuracies of about 1-2%, and dielectric constants are provided. Detailed documentation and error estimates are available in separate reports for most of the fluids. Work is underway to allow a variety of alternative equations of state to be included, such as those which integrate properties specified along the phase boundary. Accurate equations of this form have been established for such important fluids as toluene, benzene, and methanol.

17. Studies of the Properties of Natural-Gas Mixtures

T.J. Bruno, J.W. Magee, J.E. Mayrath, C.D. Holcomb, W.M. Haynes, J.B. Howley, and J.F. Ely (Colorado School of Mines)

The Thermophysics Division has been engaged in a comprehensive experimental and theoretical research program for two decades to provide the natural gas industry and the rate payer with the validated property data needed for custody transfer transactions, for energy optimization in gas industry operations, and for the design and control of gas processes. This work has been supported primarily by GRI.

A major focus of this work during the past year has been in the area of trace contaminants in natural gas, especially halogenated hydrocarbons of relatively high molecular mass. A program of fundamental research geared toward the separation of these materials from the pipeline system is currently in place. We have built two separate apparatus to measure the vapor pressures of these materials by the gas-saturation method. With these apparatus, measurements on six heavy contaminants have been completed at five temperatures. In the course of the vapor-pressure work, advances have been made in the chemical analysis of heavy chlorinated hydrocarbons. These contributions include development of analytical methods and specialized instrumentation. In addition to the vapor-pressure research, the vapor-liquid equilibria of heavy chlorinated hydrocarbons in a representative natural gas pipeline situation have been studied. The pipeline condition is simulated by a gas phase consisting of methane and a condensate phase consisting of 2,3-dimethyl pentane. The trace contaminant is spiked into the condensate, and the two-phase system is allowed to equilibrate. The solubility of the contaminant in both phases is measured as a function of temperature and pressure. An investigation of the enthalpy of adsorption of these trace contaminants on typical pipeline construction materials is planned.

NIST is a major participant in an international round-robin series of PVT measurements on five representative natural gas mixtures. This project, which has been sponsored and

managed by GRI, is a cooperative effort between U.S. and European interests in the natural gas industry. Other participants in the project include Texas A&M University in the U.S. and Ruhrgas, van der Waals Laboratory, Gasunie, and Gaz de France in Europe. The mixtures were prepared at NIST; PVT measurements were performed at NIST, Ruhrgas, van der Waals Laboratory, and Texas A&M University; and the data evaluation is being carried out at the van der Waals Laboratory. The primary objective is to provide a validated set of PVT standard reference data (uncertainty of $\pm 0.05\%$) for natural gas mixtures for custody transfer transactions. These data will establish the state-of-the-art of PVTx measurements on gas mixtures.

The major objectives of this study have been satisfied, and in some cases, exceeded. For example, the uncertainty of the reference data set in the major region of custody transfer, i.e., from 250 to 350 K at pressures to 12 MPa, is estimated to be 0.035%. At pressures to 36 MPa, the uncertainty is estimated to be less than 0.1%. The agreement between the experimental values of the compressibility factor and those calculated from custody transfer equations of state in the U.S. and Europe is approximately 0.03% in the major region of custody transfer. The results of this project will be published as a NIST Monograph.

In a related project sponsored by GPA, density measurements are being carried out on natural gas liquid components and mixtures. The purpose of this work is to improve the accuracy of ASTM and API standards for volume correction factors involved in custody transfer calculations for natural gas liquids. The experimental work is being performed at NIST, while the modeling is being done at the Colorado School of Mines. Saturated liquid density measurements have been carried out on propane, normal butane, normal pentane, isopentane, and isohexane at temperatures from 310 to 420 K. Measurements are in progress on binary mixtures of ethane and propane and planned for binary mixtures of propane, butane, and pentane.

18. Development of New Measurement Technologies for Thermophysical Properties

R.F. Chang, N.V. Frederick, W.M. Haynes, R.F. Kayser, J.W. Magee, M.O. McLinden, M.R. Moldover, G. Morrison, R.A. Perkins, and L.A. Weber

In late 1990, the Division initiated a five-year program with the Department of Energy to construct eight new thermophysical properties apparatus. This program is the continuation of an effort begun in the early 1980s to improve the thermophysical property measurement capabilities of the U.S. The new apparatus will extend the existing state of the art for property measurements and make it possible to study complex fluid systems that are inaccessible at present, including highly polar, electrically conducting, and reactive fluids. The measurement capabilities under development include: (1) Thermal Conductivity Apparatus, which will allow studies of the thermal conductivity and thermal diffusivity of electrically conducting fluids such as aqueous solutions and highly polar liquids such as

refrigerants, (2) Vibrating Wire Viscometer, which will make it possible to obtain highly accurate data at high temperatures far more routinely than is the case at present, (3) Dual-Sinker Densimeter, which will yield standard-reference-quality pressure-volume-temperature data over a wide range with a single apparatus, (4) High-Temperature Vibrating Tube Densimeter, which will extend the range and applications of this technique to much higher temperatures than are accessible at present, (5) Dynamic Phase Equilibria Apparatus, which will be ideal for characterizing fluids in the important temperature range from -50 to +150 °C, (6) Apparatus for Dilute Solutions, which will be suitable for measuring infinite dilution activity coefficients, (7) Total-Enthalpy Flow Calorimeter, which will allow accurate characterizations of reactive fluids or chemically unstable at high temperatures, and (8) Dielectric Constant Apparatus, which will make it possible to obtain molecular dipole moments and polarizabilities, which are needed to develop reliable models for the thermophysical properties of polar fluids and mixtures that contain highly polar components.

The High-Temperature Vibrating Tube Densimeter illustrates the quality of the instruments under development and the technical challenges involved. The objective of this project is to develop a precise, easy-to-use densimeter that works at temperatures up to 400 °C. As in the case of commercially available vibrating tube densimeters, the sample in our densimeter is confined to the interior of a continuous, stainless-steel tube. The tube is caused to oscillate in a bending mode and the density of the sample is determined by the change that it causes in the resonance frequency of the mode under study. However, in contrast to commercial densimeters, our densimeter does not use cements, glues, or polymer insulations of any kind. The current design also has the following unique features: (1) the use of a current passing through the tube to cause the tube to oscillate in the field of a permanent magnet, (2) the use of the voltage induced in the tube by its oscillation in the field to detect the oscillation, (3) the optional use of higher frequency modes of oscillation than the lowest bending mode of the tube, and (4) the optional use of a bridge arrangement in the detection circuitry that incorporates a non-oscillating portion of the tube to compensate for the temperature dependence of the electrical impedance of the tube. During the past year, a prototype densimeter was constructed and tested. Instabilities in its performance were traced to the use of screws to fasten components together, and all but two screws were replaced with welds. Following this, the densimeter was tested to 450 °C in a furnace acquired for the purpose. Although the densimeter continued to function at 450 °C, its resonance frequencies drifted upward the equivalent of 100 kg/m³ during the first few hours. Such a large change could result only from a change in the shape of the stainless-steel tube that is the key element of the densimeter. (Oxidation of the tube would lead to a reduction in the resonance frequencies.) Further measurements indicated a continued but much slower aging of the densimeter. We are investigating possible sources of this aging as well as the performance of a second densimeter. We also are designing a third densimeter with smaller supports that will result in faster thermal equilibration of the densimeter. Faster equilibration will permit faster acquisition of data.

In addition to these projects, we have made considerable progress on the automated detection of bubble and dew points based on capacitance measurements. Using a concentric-cylindrical capacitor designed originally by Younglove and Straty, we have studied three mixtures of carbon dioxide and ethane along many isochores. For each isochore, the temperature was ramped downward under computer control, and the temperature, pressure, and capacitance were recorded. The onset of phase separation was detected easily with very high resolution and found to be in good agreement with known results. Encouraged by this, we are vigorously developing this approach to studying phase equilibria in hydrocarbon mixtures.

19. Neutron Scattering Studies of the Structure of Fluids

H.J.M. Hanley, G.C. Straty, C.F. Zukoski (Univ. of Illinois), D.J. Evans (Australian National Univ.), and J. Barker (Australian National Univ.)

Of the common experimental probes of fluid microstructure, neutrons are advantageous because their scattering by nuclei makes isotopic substitution a tool. With selective substitution of deuterium for hydrogen in a molecule or solvent, one can monitor only those parts of the molecule or solution that one wishes to see. This technique of contrast matching was used in two experiments carried out this year at the NIST Cold Neutron Research Facility. The first set of experiments was carried out in collaboration with the University of Bristol on dilute colloidal suspensions in equilibrium. The second set was performed on dense suspensions under shear, using the shearing cell that we constructed for the Cold Neutron Research Facility in 1991. In both cases, we worked with aqueous solutions of hydrogenated polystyrene and deuterated polystyrene particles and "matched out" one of the components by adjusting the relative amounts of D₂O and H₂O in the solvent. From the measured partial structure factors, we determined the microstructure of the suspension. Parallel studies on conventional mixtures were initiated at the Los Alamos Neutron Center to explore the connection between the microstructure of simple mixtures and their non-ideal behavior.

An investigation of the structure of simple liquids under shear also was completed. The study combined elements of computer simulation and neutron scattering. A nonequilibrium molecular dynamics method was used to simulate the behavior of a dense model liquid under isothermal conditions at high shear rates. The algorithm introduced a thermostat that made no assumptions about the three-dimensional, time-dependent form of the streaming velocity of the fluid. With the form of the streaming velocity partially or wholly constrained, we found evidence for the existence of the so-called reentrant-solid, or string, phase that has been observed in previous simulations. The phase disappeared when the constraints were removed. Small angle neutron scattering data were obtained for a sheared colloidal suspension and presented alongside the simulation results. We found no evidence of a steady-state shear-induced structure in the suspension, even at shear rates 100 times that needed to melt the lattice.

A program has been started with Exxon to investigate the structure of 'living' polymers under shear. Living polymers arise when small spherical micelles form wormlike macromolecules that can grow, break, and reform. Studies of their growth rate and orientation under shear have been the focus of the program thus far. A second effort has been initiated to study the adsorption of organic materials on clay, and results were obtained for the adsorption of lysine on montmorillonite. We plan to expand these studies in the coming year.

20. Properties of Aqueous Solutions at High Temperatures and Pressures

J.M.H. Levelt Sengers, J.S. Gallagher, M.L. Huber, and D.G. Friend

In collaboration with the Process Measurements Division, the Division has initiated work related to a new technology for destroying hazardous or toxic waste. This technology is called Supercritical Water Oxidation (SCWO) and is based on the fact that organic and certain inorganic materials can be destroyed at the relatively low temperature of water just above its critical point of 374 °C. However, it has become clear that the standard techniques for describing even non-reacting aqueous solutions become awkward or useless in the range where water is highly compressible, that is, at temperatures above 300 °C and at densities below twice the critical density. In addition, to design SCWO reactors and processes, it is necessary to know at least the phase boundaries of the multicomponent systems of interest from room temperature through the supercritical regime. Although limited information is available for some binary aqueous systems, this is not the case for multicomponent systems, particularly when salts are present.

To begin to address these problems, the Division is developing accurate thermodynamic models for selected water-gas binary mixtures. These models are needed to develop generalizations for multicomponent systems and ultimately to produce a reliable and useful data base for SCWO processes. During the past year, work on the thermodynamic properties of high-temperature CO₂ in water has been completed and a paper has been written and accepted for publication in the Journal of Physical and Chemical Reference Data. The model for the Helmholtz free energy is based on the principle of generalized corresponding states, with the NBS/NRC Steam Tables as the reference state for pure water. Inputs to the model were data for the critical line of the mixture, apparent molar volume and PVT_x behavior in supercritical water, phase boundaries, excess enthalpies, and mixture second virial coefficients. The model describes the thermodynamic properties of mixtures with up to 30 mol% composition CO₂ in a large range of temperatures and pressures around the critical point of water. In addition to the work on CO₂, a database also was assembled for N₂ in water at high temperatures. Model parameters were chosen to fit the critical line, and tests to other types of data indicated that only modest further adjustments will be needed. When the work on N₂ is completed, work on O₂ will begin.

21. Supercritical Fluid Extraction of Bioproducts

T.J. Bruno, B.N. Hansen, and Jose Coelho (Instituto Superior Tecnico, Portugal)

During the past five years, there has been renewed interest in supercritical fluid extraction for industrial applications, but the systems must be chosen carefully. The best candidates are high-cost, low-volume commodities that require the use of nontoxic solvents in processing. These materials include natural products, pharmaceuticals, flavors, foods, and essential oils. The Division's past research in this area produced an economical design for the extraction of beta-carotene from aqueous solution, and a patent on a novel separator that operates in continuous rather than batch mode. The research now has focused on taxol, an anti-cancer drug; capsaicin, a drug used for the treatment of shingles; several naturally-occurring sterols with pharmaceutical applications; and phospholipids, which are of interest in the development of a supercritical fluid sterilization process (since phospholipids are an important structural component in the cell walls of many important disease-causing organisms). Fundamental measurements of vapor pressure and supercritical fluid solubility needed for process design have been completed on these important and expensive solutes. We use carbon dioxide as a reference fluid in the solubility studies and to evaluate the performance of other fluids. The other fluids include the alternative refrigerants, and we have been able to exploit the Division's extensive research program in that area.

22. Properties of Solids and Liquids at Very High Temperatures

A. Cezairliyan, J.L. McClure, A.P. Müller, and R.A. MacDonald

In this area, the Division develops new techniques and performs measurements of selected thermophysical properties of electrically-conducting materials (in solid and liquid phases) at high temperatures (1500-5000 K). This requires subsecond-duration (millisecond and microsecond-resolution) pulse heating techniques to make measurements above the limits of conventional steady-state methods. The research output serves high-temperature technologies related to spacecraft, nuclear reactors, engines, weaponry, effects of powerful lasers, materials processing, reference materials, reference data, and validation of theoretical models in related areas.

During the past year, the development of a new method for thermal conductivity measurements was completed. The thermal conductivity of tungsten in the temperature range 1800-2800 K was determined from the measurements of the transient temperature distribution in the specimen during its rapid resistive self-heating. This new technique promises to be an accurate method for thermal conductivity measurements at high temperatures where conventional techniques fail.

As part of the effort to establish practical high temperature reference points, the radiance temperature of tungsten at its melting point was measured at six wavelengths in the range 400-900 nm. Results on tungsten are especially significant because it has the highest melting point (3695 K) among the metallic elements.

The heat of fusion of tantalum was accurately measured with the microsecond resolution system as a part of the continuing effort to obtain reliable thermophysical data on high temperature metals near their melting points.

Possible future directions include the development of new methods and the performance of measurements of the thermophysical properties of advanced alloys used and intended to be used in castings in the aerospace industry. This will require measurements in both the solid and liquid phases and the development of measurement techniques applicable below 1500-2000 K.

C. Outputs and Interactions (Thermophysics Division)

1. Publications

- Arp, V.D., McCarty, R.D., and Friend, D.G., "Thermophysical Properties of Helium-4 from 0.8 to 1500 K with Pressures to 2000 MPa," NIST Technical Note 1334 - Revised (in press).
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- Bruno, T.J., "Vortex Cooled Syringe for Chromatographic Injection of Volatile Liquids," *Anal. Chem.* (in press).
- Bruno, T.J., Nieto de Castro, C.A., Hamel, J.F., and Palavra, A.M.F., "Supercritical Fluid Extraction of Biological Products," *Sep. Proc. Biol. Prod.* (in press).
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- Defibaugh, D.R., Goodwin, A.R.H., Morrison, G., and Weber, L.A., "Thermodynamic Properties of 1,1-Dichloro-1-Fluoroethane (R141b)," *Fluid Phase Equil.* (in press).
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- Mountain, R.D. and Thirumalai, D., "Loss of Ergodicity in Glassy Systems," in Proc. of the International Symposium on Slow Dynamics in Condensed Matter, Fukuoka, Japan, 165-172 (1992).
- Mountain, R.D., "Relationship Between the Fluctuation Metric and the Non-Ergodicity Parameter: Incoherent Scattering Function," Physica A (in press).

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- Thirumalai, D. and Mountain, R.D., "Activated Dynamics, Loss of Ergodicity, and Transport in Supercooled Liquids," Phys. Rev. A (in press).
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- Tilford, C.R., "New Directions in Vacuum Measurements at NIST," in Proc. of the 1992 NCSL Workshop and Symposium, Washington, DC, 583-592 (1992).
- Van Poolen, L.J., Niesen, V.G., Holcomb, C.D., and Outcalt, S.L., "Determination of Critical Densities from Coexisting Density Data: Application to Refrigerants R22, R134a, and R124," Fluid Phase Equil. (in press).
- Van Poolen, L.J., Niesen, V.G., and Rainwater, J.C., "An Experimental Method for Obtaining Critical Densities for Binary Mixtures: Application to Ethane + n-Butane," Fluid Phase Equil. 66, 161-185 (1991).
- Weber, L.A., "Ebulliometric Measurement of the Vapor Pressures of R123 and R141b," Fluid Phase Equil. (in press).
- Weber, L.A., "The CO₂ + Ethane System: Virial Coefficients at 320 K and Near-Critical Isochores," Int. J. Thermophysics (in press).
- Weber, L.A., "Criteria for Establishing Accurate Vapor Pressure Curves," in Proc. of the International Refrigeration Conference on Energy Efficiency and New Refrigerants, West Lafayette, IN, 463-472 (1992).
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- Zhang, K.C., Briggs, M.E., Gammon, R.W., and Sengers, J.M.H. Levelt, "The Susceptibility Critical Exponent of a Nonaqueous Ionic Binary Near a Consolute Point," J. Chem. Phys. (in press).

2. Talks

- Berg, R.F., "Wide-Bandwidth Viscometer for Low Viscosity Fluids," Annual Meeting of the American Physical Society, Indianapolis, IN, March 17, 1992.
- Bruno, T.J., "Industrial Supercritical Fluid Extraction of Beta-Carotene," Organic Analytical Research Division Seminar, NIST, Gaithersburg, MD, November 11, 1991. Invited
- Bruno, T.J., "Industrial Supercritical Fluid Extraction," NIST-Consortium on Automated Analytical Laboratory Systems (CAALS) Conference, Gaithersburg, MD, November 12, 1991. Invited
- Bruno, T.J., "Measurement of the Vapor Pressures of PCBs," Gas Research Institute Meeting, Chicago, IL, January 22, 1992. Invited
- Bruno, T.J., "The PCB Property Program at NIST," Gas Research Institute Thermophysical Properties Contract Review Meeting, Anaheim, CA, March 12, 1992. Invited
- Bruno, T.J., "Physicochemical Measurements for the Separation of PCBs from Pipelines," Gas Research Institute Meeting, Chicago, IL, May 13, 1992. Invited
- Bruno, T.J., "Chemical Analysis of Alternative Refrigerants: Spectroscopic Methods," ASHRAE National Meeting, Baltimore, MD, June 30, 1992.
- Bruno, T.J., "Chemical Analysis of Alternative Refrigerants: Separation Methods," ASHRAE National Meeting, Baltimore, MD, June 30, 1992.
- Bruno, T.J., "Chemical Analysis of Alternative Refrigerants," Department of Chemistry, Georgetown University, Washington, DC, June 30, 1992. Invited
- Cezairliyan, A., "A Dynamic Technique for Measuring Thermal Conductivity at High Temperatures," Third Workshop on Subsecond Thermophysics, Technical University of Graz, Graz, Austria, September 17, 1992.
- Defibaugh, D.R., "Compressed Liquid Densities, Saturated Liquid Densities, and Saturation Pressures of Mixtures Difluoromethane + 1,1,1,2 Tetrafluoroethane and Difluoromethane + 1,1-Difluoroethane," International Refrigeration Conference, Purdue University, West Lafayette, IN, July 16, 1992.
- Dittmann, S., Vacuum Calibration Workshop, NIST, Gaithersburg, MD, May 1992.
- Doty, S.W., "High Pressure Gas Calibration at NIST," 1992 Navy Metrology Research and Development Requirements Conference, Annapolis, MD, June 10, 1992. Invited

Ehrlich, C.D., "Intercomparison of Hydraulic Pressure Measurements to 28 MPa Using a Single Piston Gage in the Controlled-Clearance, Reentrant and Simple Configurations," XIII AIRAPT Conference on High Pressure Science and Technology, Bangalore, India, October 7, 1991. Invited

Ehrlich, C.D., "Latest Developments in Static Pressure Measurements at NIST," NCSL Region 3 Semi-Annual Meeting, NIST, Gaithersburg, MD, October 24, 1991. Invited

Ehrlich, C.D., "Pressure Measurement Uncertainty Using Deadweight Piston Gages," 1992 Measurement Science Conference, Symposium, and Workshop, Anaheim, CA, January 31, 1992. Invited

Ehrlich, C.D., "High Pressure Measurement at NIST and Cooperative Activities between NIST and IMGC," Joint Italian - U.S. Measurements Seminar, Torino, Italy, May 6, 1992. Invited

Filippelli, A.R., "Some Accuracy, Relative Response to Different Gases, Repeatability, and Pumping Speed Measurements for a Group of Inverted Magnetron Cold Cathode Gages," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 12, 1991.

Friend, D.G., "Interactive Computation of Thermophysical Properties for Supercritical Aqueous Systems," Workshop on Federal Programs Involving Supercritical Water Oxidation, NIST, Gaithersburg, MD, July 6, 1992.

Gillis, K.A., "Dielectric Detection of Phase Equilibria," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, August 21, 1992.

Gillis, K.A., "Thermophysical Properties of Gaseous 1-Chloro-1,2,2,2-Tetrafluoroethane and 2-Difluoromethoxy-1,1,1-Trifluoroethane from Acoustic Measurements," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, August 20, 1992.

Goodwin, A.R.H., "Thermodynamic Properties of Alternative Refrigerants," Department of Chemistry, University of Florida, Gainesville, FL, November 4, 1991. Invited

Goodwin, A.R.H., "Thermophysical Properties of Alternative Refrigerants," Department of Chemical Engineering, Texas A&M University, College Station, TX, February 24, 1992. Invited

Hanley, H.J.M., "Neutron Scattering from Colloids," Reactor Radiation Division Seminar, NIST, Gaithersburg, MD, November 21, 1991.

- Hanley, H.J.M., "Structures of Mixtures," 18th Statistical Physics (STATPHYS) Meeting, Berlin, Germany, August 4, 1992. Invited
- Hanley, H.J.M., "Structures of Mixtures," Research School of Chemistry, Australian National University, Canberra, Australia, February 6, 1992. Invited
- Hanley, H.J.M., "Neutron Scattering Studies," Department of Physics, University of Western Australia, Perth, Australia, February 20, 1992. Invited
- Hanley, H.J.M., "Properties of Liquid Mixtures," Department of Physics, Murdoch University, Perth, Australia, February 21, 1992. Invited
- Hansen, B.N., "Supercritical Fluid Thin Film Deposition," Thermophysics Division Seminar, NIST, Boulder, CO, January 31, 1992.
- Haynes, W.M., "PVT Reference Data for Natural Gas Mixtures," Gas Research Institute Thermophysical Properties Contract Review Meeting, Anaheim, CA, March 12, 1992. Invited
- Haynes, W.M., "Experimental Measurements and Models for Volume Correction Factors in Natural Gas Liquids," Gas Processors Association 71st Annual Convention, Anaheim, CA, March 16, 1992. Invited
- Holcomb, C.D., "Improved Differential Bubble Pressure Surface Tension Measurements," AIChE Annual Meeting, Los Angeles, CA, November 20, 1991.
- Hyland, R.W., "Recommended Practices for the Calibration and Use of Capacitance Diaphragm Gages as Transfer Standards," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 12, 1991.
- Hyland, R.W., "Using Liquid Column Manometers--Considerations and Applications," 1992 Measurement Science Conference, Symposium, and Workshop, Anaheim, CA, January 31, 1992. Invited
- Looney, J.P., "Vacuum Standards at NIST," Department of Physics, Slippery Rock University, Slippery Rock, PA, October 17, 1991. Invited
- Looney, J.P., "The Effect of Upstream Tubulation on the Conductance of an Ideal Orifice," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 11, 1991.
- Looney, J.P., "New Vacuum Standards at NIST," 1992 Measurement Science Conference, Symposium, and Workshop, Anaheim, CA, January 31, 1992. Invited

- Mayrath, J.E., "The Physics and Chemistry of Benchrest Shooting," Thermophysics Division Seminar, NIST, Boulder, CO, December 13, 1991.
- McLinden, M.O., "Replacing the CFCs," NIST Boulder Laboratories Colloquium Series, Boulder, CO, November 6, 1991.
- McLinden, M.O., "Thermophysical Properties of Alternative Refrigerants for Centrifugal Compressors," ASHRAE Winter Meeting, Anaheim, CA, January 28, 1992.
- McLinden, M.O., "Thermodynamic Properties of R134a," International Refrigeration Conference, Purdue University, West Lafayette, IN, January 28, 1992.
- McLinden, M.O., "Replacing the CFCs," Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, CO, April 4, 1992.
- Miiller, A.P., "Radiance Temperatures (in the Wavelength Range 519-906 nm) of Tungsten at Its Melting Point by a Pulse-Heating Technique," Third Workshop on Subsecond Thermophysics, Technical University of Graz, Austria, September 17, 1992. Invited
- Miiller, A.P., "Radiance Temperatures (in the Wavelength Range 521-906 nm) of Molybdenum at Its Melting Point by a Pulse-Heating Technique," Seventh International Symposium on Temperature, Toronto, Canada, May 1, 1992.
- Miiller, A.P., "Radiance Temperature and Normal Spectral Emissivity of Metals at Their Melting Point as Possible Reference Values," Seventh International Symposium on Temperature, Toronto, Canada, April 28, 1992.
- Moldover, M.R., "Thermophysical Properties Measurements and Instrumentation at NIST," BP America, Houston, TX, November 6, 1991. Invited
- Moldover, M.R., "Measurement of Thermophysical Properties of Gases Using Acoustical Techniques," Second Workshop on Mass Flow Controllers, Austin, TX, January 31, 1992. Invited
- Moldover, M.R., "Thermophysical Properties of Alternative Refrigerants: Measurements, Estimates, and Packaging at NIST," Department of Chemical Engineering, Imperial College, London, England, March 11, 1992. Invited
- Moldover, M.R., "Precise Acoustic Measurement of Thermophysical Properties of Gases," Annual Meeting of the American Physical Society, Indianapolis, IN, March 17, 1992. Invited

- Moldover, M.R., "Research on CFC Replacements in the Thermophysics Division," Organic Analytical Research Division Seminar, NIST, Gaithersburg, MD, April 22, 1992. Invited
- Morrison, G., "Azeotropy in Refrigerant Mixtures," 1991 Annual Meeting of the German Refrigeration and Air Conditioning Society, Berlin, Germany, November 22, 1991. Invited
- Morrison, G., "Azeotropy in Refrigerant Mixtures," Technical University of Delft, Delft, The Netherlands, November 25, 1991. Invited
- Morrison, G., "Physical Chemistry and Choosing New Refrigerants," American Chemical Society Student Affiliates, Mount Saint Mary's College, Emmitsburg, MD, March 4, 1992. Invited
- Morrison, G., "Picking Apples in a Shrinking Orchard: Are There New Orchards? The Search for Alternative Refrigerants," CSTL Colloquium, NIST, Gaithersburg, MD, May 20, 1992. Invited
- Mountain, R.D., "Loss of Ergodicity in Glassy Systems," 1st Tohwa University International Symposium on Slow Dynamics in Condensed Matter, Fukuoka, Japan, November 4, 1991. Invited
- Mountain, R.D., "Computer Simulation Studies of Glassy States," Polymer Division Seminar, NIST, Gaithersburg, MD, May 26, 1992. Invited
- Mountain, R.D., "Computer Simulation Investigations of Crystal Nucleation Processes," American Ceramic Society on Glass and Optical Materials Meeting, Stone Mountain, GA, August 17, 1992. Invited
- Outcalt, S.O., "Catalytic Cracking Detector for Gas Chromatography," Thermophysics Division Seminar, NIST, Boulder, CO, March 6, 1992.
- Perkins, R.A., "Thermal Radiation Effects in Transient Hot-Wire Measurements of Refrigerant Thermal Conductivity," IUPAC Subcommittee on Transport Properties Meeting, Rostock, Germany, September 14, 1992.
- Rainwater, J.C., "A Theoretical Analysis of Double Retrograde Vaporization," AIChE Annual Meeting, Los Angeles, CA, November 20, 1991.
- Rainwater, J.C., "Calculation of Collision Integrals Arising in Moderately Dense Gas Kinetic Theory," Theoretical Chemistry Seminar, University of British Columbia, Vancouver, B.C., Canada, July 15, 1992. Invited

- Rainwater, J.C., "Theory of Linear Density Corrections to Viscosity and Thermal Conductivity of Gases," 18th International Symposium on Rarefied Gas Dynamics, Vancouver, B.C., Canada, July 28, 1992.
- Rainwater, J.C., "Calculation of Entropy, Enthalpy, and Free Energy Differences of Near-Critical Mixtures with the Modified Leung-Griffiths Model," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, August 21, 1992.
- Ripple, D., "Flow of Microemulsions through Microscopic Pores," Annual Meeting of the American Physical Society, Indianapolis, IN, March 19, 1992.
- Ripple, D., "Design and Performance of a High Pressure Capillary Viscometer," Thermophysics Division Seminar, NIST, Gaithersburg, MD, May 18, 1992. Invited
- Schmidt, J.W., "Investigation of Effects on Drag and Area Using a Three Piston Gage Apparatus," NCSL Workshop and Symposium, August 5, 1992.
- Sengers, J.M.H. Levelt, "Critical Behavior of Ionic Fluids," Chemistry Department, University of Bremen, Bremen, Germany, November 4, 1991. Invited
- Sengers, J.M.H. Levelt, "Critical Behavior of Ionic Fluids," Physical Chemistry Colloquium, University of Karlsruhe, Karlsruhe, Germany, November 11, 1991. Invited
- Sengers, J.M.H. Levelt, "Supercritical Steam: Technology, Environment, Science," Physics Department, Technical University of Aachen, Aachen, Germany, November 25, 1991. Invited
- Sengers, J.M.H. Levelt, "Thermophysikalische Eigenschaften von verdünnten Lösungen in nahkritischen Lösungsmitteln," Physical Chemistry Colloquium, Ruhr Universität Bochum, Germany, January 31, 1992.
- Sengers, J.M.H. Levelt, "Critical Behavior of Ionic Fluids," Statistical Physics Seminar, University of Maryland, College Park, MD, May 11, 1992. Invited
- Sengers, J.M.H. Levelt, "Thermophysical Properties of Supercritical Multicomponent Aqueous Mixtures," Workshop on Federal Programs Involving Supercritical Water Oxidation, NIST, Gaithersburg, MD, July 7, 1992. Invited
- Sengers, J.M.H. Levelt, "Supercritical Water Oxidation, A New Technology," Gordon Research Conference on Water, The Holderness School, Holderness, NH, August 3, 1992.

Sengers, J.M.H. Levelt, "Supercritical Steam: Science, Energy, Environment," Honorary Doctor's Lecture, Technical University of Delft, Delft, The Netherlands, September 18, 1992. Invited

Straty, G.C., "Neutron Scattering from Colloids," Reactor Radiation Division Seminar, NIST, Gaithersburg, MD, November 21, 1991.

Tison, S.A., "Vacuum Calibrations with Water Vapour: Initial Results," 38th National Symposium of the American Vacuum Society, Seattle, WA, November 19, 1991.

Tilford, C.R., "Torricelli's Legacy: Vacuum Measurements and Standards at NIST," Joint Italian-U.S. Measurements Seminar, Torino, Italy, May 5, 1992.

Tilford, C.R., "Characteristics of Partial Pressure Analyzers," SPIE 1992 International Symposium on Optical Applied Science and Engineering, San Diego, CA, July 27, 1992.

Tilford, C.R., "Calibration of MSX Contamination Study Vacuum Gages," SPIE 1992 International Symposium on Applied Science and Optical Engineering, San Diego, CA, July 31, 1992.

Tilford, C.R., "What's New in Vacuum Measurements at NIST," NCSL Workshop and Symposium, Washington, D.C., August 5, 1992.

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Development of a Primary Pressure Standard for Gage and Absolute Pressure Using Different Gases in the Range 2.5 to 175 kPa, C.D. Ehrlich
DH Instruments, Inc. (CRADA)

4. Patent Awards and Applications

Bruno, T.J., Apparatus and Method for Evaporative Sample Concentration (Awarded September 1992).

Bruno, T.J., A Simple and Efficient Low Temperature Sample Cell for Infrared Spectrometry (Submitted March 1992).

Morrison, G., Azeotropic Refrigerant Comprising Bis-(Difluoromethyl) Ether and 1,1,2-Trifluoroethane (Submitted February 1992).

Morrison, G., Azeotropic Mixture of Isobutane and 1,1,1,2-Tetrafluoroethane (Submitted April 1992).

5. SRM Activities

None

6. SRD Activities

NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Data Base (REFPROP), Upgrade

NIST Thermophysical Properties of Hydrocarbon Mixtures Data Base (SUPERTRAPP), Upgrade

NIST Mixture Properties Data Base (DDMIX), Upgrade

NIST Thermophysical Properties of Fluids Data Base (MIPROPS), Upgrade

7. Calibrations

Calibration services (pressure, vacuum, and leakrate) have been provided for the following organizations:

Aerojet General Corp.

Allied Signal

Argonne National Laboratory

Atmospheric Sciences Laboratory

Ball Aerospace Systems Group

Boeing Defense and Space Group

Bonneville Power Administration

Carrier Corp.

Center for Measurement Standards

Consumer Power Co.

DH Instruments Inc.

Eastman Kodak Co.

EG&G Mound Applied Technology

EG&G Energy Measurements

General Motors Corp.

Gulf States Utilities Co.

Gulf States Utilities Co.

Hughes Aircraft Co.

IMO Delaval Inc.

LDS Vacuum Products Inc.

Leybold Inficon, Inc.

Lockheed Missiles and Space Co.

Martin Marietta Corp.

Martin Marietta Energy Systems

MKS Instruments Inc.

NASA Kennedy Space Flight Center

NASA Langley Research Center

Navy Primary Standards Laboratory East

Navy Primary Standards Laboratory West

Newark Air Force Base

Philadelphia Electric Co.

Rockwell International

Sandia National Laboratory

TRW Space and Defense Sector

U.S. Army TMDE Activity, Redstone Arsenal

Varian

VEECO Instruments Inc.

Westinghouse Savannah River Co.
Westinghouse Hanford Co.
Willson Scientific Glass Inc.

8. Committee Assignments

T.J. Bruno

NIST Boulder Library Advisory Committee
NIST Shops Advisory Committee
NIST Research Advisory Committee
CSTL Boulder Colloquium Committee (Chairman)

A. Cezairliyan

International Organizing Committee, European Thermophysical Properties Conference
ASME K-7 Thermophysical Properties Committee
International Thermophysics Congress (Chairman)
International Commission on Standardization of Thermophysical Measurement Techniques
ASTM Thermophysical Properties Subcommittee
International Organizing Committee of the Subsecond Thermophysics Workshops
Organizing Committee of the Workshop on Thermophysical Properties of Molten Materials

S. Dittmann

American Vacuum Society, Technology Division (Board of Directors)
CSTL Colloquium Committee (Chairman)

C. Ehrlich

BIPM Consultative Committee for Mass and Related Quantities, Working Groups on High Pressure and Medium Pressure
ASTM Committee E07 on Nondestructive Testing
ASTM Subcommittee E07.08 on Leak Testing
AVS Calibrated Leak Subcommittee (Co-Chairman)
NCSL Recommended Practices Committee on Deadweight Standards (Chairman)

A.R. Filippelli

AVS Vacuum Technology Division (Board of Directors)
AVS Recommended Practices Committee on the Calibration of Mass Spectrometers for Partial Pressure Analysis
Journal of Vacuum Science and Technology Shop Note Award Committee (Chairman)

D.G. Friend

Director, Fluid Mixtures Data Center

J.S. Gallagher

International Association for Properties of Water and Steam, Working Group for
Thermophysical Properties

ASME Research and Technology Committee on Water in Thermal Power Systems

ASME Research Subcommittee on the Properties of Water and Steam (Secretary)

H.J.M. Hanley

ASME K-7 Thermophysical Properties Committee

W.M. Haynes

International Energy Agency Annex 18 - Thermophysical Properties of
Environmentally Acceptable Refrigerants

ASTM Committee D03 on Gaseous Fuels

M.L. Huber

Boulder Computer Users Group

Boulder Editorial Review Board

R.W. Hyland

AVS Recommended Practices Committee on the Use of Capacitance Diaphragm Gages

R.F. Kayser

Working Group on Mitigation and Adaptation Research Strategies, Committee on
Earth and Environmental Sciences, Federal Coordinating Council for Science,
Engineering, and Technology (FCCSET)

Interdepartmental Task Force on Environment and Competitiveness

J.P. Looney

CSTL Colloquium Committee

T.R. Lettieri

Optical Society of America Education Council

R.A. MacDonald

NIST Employee Advisory Committee for the Personnel Management Demonstration
Project (Chairman)

Washington Editorial Review Board

J.E. Mayrath

NIST Boulder Hazards Review Committee

M.O. McLinden

ASHRAE Technical Committee 3.1 - Refrigerants and Brines (Chairman)
ASHRAE Standards Project Committee 34 - Nomenclature and Safety Classification of Refrigerants
ASHRAE CFC Position Paper Committee
International Energy Agency Annex 18 - Thermophysical Properties of Environmentally Acceptable Refrigerants (Operating Agent/Chairman)

A.P. Miiller

ASME K-7 Thermophysical Properties Committee
ASTM Committee E37 on Thermal Measurements
ASTM Thermophysical Properties Subcommittee
Touloukian Award Subcommittee of the ASME Heat Transfer Division

M.R. Moldover

NASA Proposal Review Panel on Metals and Alloys Containerless Processing
NASA Review Panel, Fluid Dynamics Discipline Working Group
NASA Review Panel, Fundamental Processes Discipline Working Group

G. Morrison

NIST Library Subject Specialist Committee

R.D. Mountain

NIST Library Subject Specialist Committee
NIST Users Committee for Scientific Computing (Chairman)

R.A. Perkins

Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics

J.M.H. Levelt Sengers

International Association for Properties of Water and Steam (President and U.S. National Delegate)
International Association for Properties of Water and Steam, Working Group for Thermophysical Properties
International Association for Properties of Water and Steam, Working Group on Physical Chemistry of Aqueous Systems
ASME Research Committee on the Properties of Water and Steam

J.V. Sengers

ASME K-7 Thermophysical Properties Committee
ASME Research Committee on the Properties of Water and Steam
International Association for Properties of Water and Steam, Working Group for Thermophysical Properties

Program Committee of 12th International Conference on the Properties of Water and Steam (Chairman)

Touloukian Award Subcommittee of the ASME Heat Transfer Division

C.R. Tilford

Radio and Technical Commission for Aeronautics, Special Committee 150, Performance

Requirements for 100 Foot Vertical Separation of Aircraft Above Flight Level 290

BIPM Consultative Committee for Mass and Related Quantities, Medium and Low Pressure Working Groups (Chairman)

S.A. Tison

ASTM Subcommittee E07.08 on Leak Testing (Vice Chairman)

9. Editorships

A. Cezairliyan

Compendium on Thermophysical Properties Measurement Methods, Plenum Publishing Company (Editor)

International Journal of Thermophysics (Editor-in-Chief)

Journal of High Temperature Science (Editorial Board)

High Temperatures-High Pressures (Editorial Board)

H.J.M. Hanley

International Journal of Thermophysics (Editorial Board)

C.R. Tilford

Vacuum (Editorial Board)

10. Seminars

November 8, 1991

Dr. C.J. Peters, Technical University of Delft, Delft, The Netherlands, "Phase Behavior of Binary Hydrocarbon Systems of Interest for the Natural Gas Industry." (Division Sponsor: W.M.Haynes)

November 8, 1991

Dr. Th.W. de Loos, Technical University of Delft, Delft, The Netherlands, "Critical Curves in Binary and Pseudo-Binary Families." (Division Sponsor: W.M. Haynes)

November 19, 1991

Dr. K.C. McGill, Department of Chemistry, University of Florida, Gainesville, FL, "Sonic Transformed Multi-Phase Cylindrical Resonator for Steam Quality Measurements." (Division Sponsor: M.R. Moldover)

December 6, 1991

Dr. Donald H. Stedman, Brainerd Phillipson Professor of Chemistry, University of Denver, "Remote Sensing of Air Pollutant Emissions." (Division Sponsor: T.J. Bruno)

December 6, 1991

Professor Koichi Watanabe, Thermodynamics Laboratory, Department of Mechanical Engineering, Keio University, Yokohama, Japan, "Recent Progress on Thermodynamic Property Research on Alternative Refrigerants at Keio University." (Division Sponsor: R.F. Kayser)

December 9, 1991

Dr. Gianfranco Molinar, Istituto di Metrologia "G. Colonnetti", Torino, Italy, "Measurement and Calculation of the Pressure Distortion Coefficients in Simple Piston-Cylinder Units with Pressures up to 500 MPa." (Division Sponsor: C.D. Ehrlich)

December 20, 1991

Dr. Edward Gardner, Council of Engineering, Yale University, New Haven, CT, "The Use of Non-Linear Acoustics to Study and Stimulate the Coalescence of Oil Drops Surrounded by Water." (Division Sponsor: M.R. Moldover)

January 16, 1992

Dr. John K. Lauber, Member, National Transportation Safety Board, Washington, D.C., "Chemical and Physical Methods in Accident Investigation (or, How a Quarter-Mile of Rubble Yields the Cause of an Airliner Crash)." (Division Sponsor: T.J. Bruno)

January 24, 1992

Dr. Rodney Skogerboe, Professor Emeritus of Chemistry, Colorado State University, Fort Collins, CO, "Chemical Analysis of Food Products." (Division Sponsor: T.J. Bruno)

February 6, 1992

Professor William B. Krantz, University of Colorado, Boulder, CO, "Waves and Spatial Patterns in Nature." (Division Sponsor: T.J. Bruno)

February 14, 1992

Professor Albert A. Bartlett, University of Colorado, Boulder, CO, "The Forgotten Fundamentals of the Energy Crisis or Arithmetic, Population, and Energy." (Division Sponsor: T.J. Bruno)

February 21, 1992

Dr. Werner Loose, Institute for Theoretical Physics, Technical University of Berlin, Berlin, Germany, "Computer Simulation Studies on the Microscopic Origin of the Complex Rheology of Simple Model Fluids." (Division Sponsor: T.J. Bruno)

March 20, 1992

Professor Hiroyuki Nishide, Waseda University, Tokyo, Japan, "Liposome/Heme as a Totally Synthetic Blood Substitute." (Division Sponsor: T.J. Bruno)

April 10, 1992

Jeffrey R. Fox, Foxcom, Boulder, CO, "A Thermophysical Property Calculator Embedded in a Commercial Spreadsheet." (Division Sponsor: T.J. Bruno)

April 17, 1992

Ms. Janine Anderson, Speakers for a Sustainable Future, Arvada, CO, "Greening Your Business." (Division Sponsor: T.J. Bruno)

May 1, 1992

Dr. William T. Foreman, National Water Quality Laboratory, United States Geological Survey, Arvada, CO, "Solid Phase and Continuous Flow Liquid-Liquid Extraction Methods for Trace Agricultural Pollutants in Water." (Division Sponsor: T.J. Bruno)

May 6, 1992

Dr. Lukasz A. Turski, Institute for Theoretical Physics, Polish Academy of Sciences, Warsaw, Poland, "The Case of Hydrodynamics in $d = 2 + 1$ Dimensions." (Division Sponsor: R.D. Mountain)

May 8, 1992

Professor J.B. Joshi, University of Bombay, India, "Flow Fields and Mixing in Stirred Vessels." (Division Sponsor: T.J. Bruno)

May 8, 1992

Dr. James A. Given, Department of Chemistry, State University of New York, Stony Brook, NY, "Continuum Percolation and Clustering in Electrolytes." (Division Sponsor: J.M.H. Levelt Sengers)

May 13, 1992

Professor M. Anisimov, Chairman, Physics Department, Oil and Gas Research Institute, Russian Academy of Sciences, Moscow, Russia, "Critical-Point Universality: How Does it Work in Binary Mixtures Near Plait Points?" (Division Sponsor: J.M.H. Levelt Sengers)

May 15, 1992

Dr. Robert V. Collins, Roy F. Weston, Inc., Lakewood, CO, "In-the-Field Analytical Methods for PCB's." (Division Sponsor: T.J. Bruno)

May 22, 1992

Ms. Janine Anderson, Speakers for a Sustainable Future, Arvada, CO, "Recycling and Water Conservation." (Division Sponsor T.J. Bruno)

June 12, 1992

Dr. Anna Emery, Organic Analytical Research Division, NIST, Gaithersburg, MD, "Supercritical Fluid Extraction of Environmental Analytes from Clays and Soils." (Division Sponsor: T.J. Bruno)

July 17, 1992

Mr. David French, Los Alamos National Laboratory (LANL), Los Alamos, New Mexico, "Technical and Legal Aspects of the Rocky Flats Cleanup: The Perspective of LANL." (Division Sponsor: T.J. Bruno)

July 24, 1992

Dr. Clement Yonker, Battelle-Pacific Northwest Laboratory, Richland, WA, "Supercritical Fluid Extraction and Spectroscopy." (Division Sponsor: T.J. Bruno)

July 27, 1992

Professor H. Weingartner, Department of Chemistry, University of Karlsruhe, Karlsruhe, Germany, "Liquid-Liquid Phase Transitions in Electrolyte Solutions." (Division Sponsor: J.M.H. Levelt Sengers)

July 31, 1992

Mr. Jose A.P. Coelho, Instituto Superior Tecnico, Lisbon, Portugal, "Studies in Supercritical Fluid Extraction: Sterols." (Division Sponsor: T.J. Bruno)

August 7, 1992

Dr. Lambert J. Van Poolen, Calvin College, Grand Rapids, MI, "The Use of Coexistence Density Derivative Information to Determine Critical Densities and Temperatures." (Division Sponsor: T.J. Bruno)

August 14, 1992

Professor J.P.M. Trusler, Department of Chemical Engineering, Imperial College, London, UK, "The Speed of Sound and Thermodynamic Properties of Gaseous Mixtures of Methane and Ethane." (Division Sponsor: M.R. Moldover)

August 24, 1992

Dr. Michael B. Ewing, Department of Chemistry, University College London, London, UK, "Thermophysical and Electric Properties of Gases Determined Using Resonators." (Division Sponsor: M.R. Moldover)

August 25, 1992

Dr. Ulrich Deiters, Department of Chemistry, Ruhr University Bochum, Bochum, Germany, "Global Phase Diagrams of Binary Fluid Mixtures." (Division Sponsor: J.M.H. Levelt Sengers)

August 27, 1992

Professor R. Fernandez-Prini, Departamento Quimica de Reactores, Comision Nacional de Energia Atomic, Buenos Aires, Argentina, "Behavior of Dilute Aqueous Solutions at High Temperatures." (Division Sponsor: D. Fernandez)

August 31, 1992

Professor H. Craubner, Max Planck Institute for Solid State Physics, Stuttgart, Germany, "Thermodynamics of Condensed Matter Based on Densimetric Measurements as a Function of Temperature." (Division Sponsor: R.F. Berg)

September 21, 1992

Dr. Peter William Sendrup, Department of Chemical Engineering, The Technical University of Denmark, Lyngby, Denmark, "Dielectric Detection of Liquid to Gas Phase Transitions." (Division Sponsor: A.R.H. Goodwin)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

February 26-28, 1992

The Thermodynamics of Advanced Compression Systems, Absorption Systems, and Their Working Fluids, University of Maryland, Engineering Research Center, College Park, MD (D.A. Didion, G. Morrison, and R. Radermacher)

April 4-9, 1992

Workshop on Standards for Process Analytical Chemistry, ANATECH, Atlanta, GA (T. Bruno)

April 22-24, 1992

Precision Measurement Workshop on the Calibration and Use of Piston Gages, NIST, Gaithersburg, MD (C.D. Ehrlich)

May 18-20, 1992

Vacuum Calibrations Using the Molecular Drag Gage, NIST, Gaithersburg, MD (S. Dittmann)

GLOSSARY

Government Agencies and Departments

AFB	Air Force Base
AFTAC	Air Force Technical Applications Center
AMMTAP	Alaska Marine Mammal Tissue Archival Project
ATP	Advanced Technology Program
CARB	Center for Advanced Research in Biotechnology (831)
CCG	Calibration Coordination Group of the Department of Defense
CRDEC	Chemical Research, Development & Engineering Center
CSTL	Chemical Science and Technology Laboratory
DARPA	Defense Advanced Research Projects Agency
DoC	Department of Commerce
DoD	Department of Defense
DoE	Department of Energy
EEEL	Electronics and Electrical Engineering Laboratory
EMAP	Environmental Monitoring & Assessment Program
EPA	Environmental Protection Agency
FBI	Federal Bureau of Investigation
IMGC	Istituto di Metrologia "G. Colennetti" (Italy)
JANNAF	Joint Army - Navy - National Aeronautics and Space Administration - Air Force
JOCG	Joint Ordnance Commanders Group
KRISS	Korea Research Institute of Standards and Science
MEL	Manufacturing Engineering Laboratory
MMS	Minerals Management Service
MSEL	Materials Science and Engineering Laboratory
NASA	National Aeronautics and Space Administration
NCAR	National Center for Atmospheric Research
NCI	National Cancer Institute
NIDA	National Institute on Drug Abuse
NIH	National Institutes of Health
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NMMTB	National Marine Mammal Tissue Bank
NOAA	National Oceanic and Atmospheric Administration
NPL	National Physical Laboratory (England)
NRC	Nuclear Regulatory Commission
NRLM	National Research Laboratory of Metrology (Japan)
NS&T	National Status and Trends
NSF	National Science Foundation

PTB	Physikalisch Technische Bundesanstalt (Germany)
SRDP	Standard Reference Data Program
SRMP	Standard Reference Materials Program
TMDE	U.S. Army Test, Measurement, and Diagnostic Equipment Support Group
USGS	U.S. Geologic Survey
VNIIM	D.I. Mendeleyev Institute for Metrology
VSL	Van Swinden Laboratorium (Netherlands)
WHOI	Woods Hole Oceanographic Institute
WRDC	Wright Research and Development Center

Associations and Committees

AAAR	American Association for Aerosol Research
ABC	Association of Biotechnology Companies
ACS	American Chemical Society
AGA	American Gas Association
AIChE	American Institute of Chemical Engineers
AIRAPT	Int'l Association for the Advancement of High Pressure Science and Technology
ANSI	American National Standards Institute
ANS	American Nuclear Society
API	American Petroleum Institute
APS	American Physical Society
ASHRAE	American Society of Heating, Refrigeration, and Air Conditioning Engineers
ASME	American Society of Mechanical Engineers
ASMS	American Society for Mass Spectrometry
ASTM	American Society for Testing and Materials
AVS	American Vacuum Society
AWWA	American Water Works Association
BIPM	International Bureau of Weights and Measures
BRDC	Biotechnology Research and Development Corporation
BRS	Biotechnology Research Subcommittee
CAALS	Consortium on Automated Analytical Systems
CAB	Consortium on Advanced Biosensors
CAP	College of American Pathologists
CARB	California Air Resources Board (835)
CHEMRAWN	Chemical Research Applied to World Needs
CLSH	Committee on Life Science and Health
CODATA	International Council of Scientific Unions Committee on Data for Science and Technology
DIPPR	Design Institute for Physical Property Data
EPRI	Electric Power Research Institute

FCCSET	Federal Coordinating Committee on Science, Engineering, and Technology
GEC	Gaseous Electronics Conference
GPA	Gas Processors Association
GRI	Gas Research Institute
IAEA	International Atomic Energy Agency
IAPWS	International Association for the Properties of Water and Steam
IBA	Industrial Biotechnology Association
IEA	International Energy Agency
IEC	International Electrotechnic Commission
IEEE	Institute of Electrical and Electronics Engineers
ISA	Instrument Society of America
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JPL	Jet Propulsion Laboratory
MRS	Materials Research Society
MSDC	Mass Spectrometry Data Center
MVMA	Motor Vehicle Manufacturers Association
NCCLS	National Committee of Clinical Laboratory Standards
NCSL	National Conference of Standards Laboratories
OIML	International Organization for Legal Metrology
SAS	Society for Applied Spectroscopy
SEMATECH	Semiconductor Industry Technology Consortium
SES	Senior Executive Service
SPIE	Society of Photo-optical Instrumentation Engineers
WHO	World Health Organization
VAMAS	Versailles Project on Advanced Materials and Standards
TWGDAM	Technical Working Group on DNA Analysis Method

Technical

1-D	One Dimensional
AC	Analog Converter
AEM	Analytical Electron Microscope
AMS	Accelerator Mass Spectrometry
ASEM	Automated Scanning Electron Microscopy/electron Probe Microscope
ATP	Adenosine Triphosphate
BHP	Basic Hydrogen Peroxide
BR	Bacteriorhodopsin
C ₁₈	Octadecylsilane
CAALS	Consortium on Automated Analytical Laboratory Systems
cAMP	cyclic AMP Receptor
CAP	Catabolite Activator Protein

CCD	Charge Coupled Device
CDG	Capacitance Diaphragm Gage
CE	Capillary Electrophoresis
CFC	Chlorofluorocarbon
CFD	Computational Fluid Dynamics
CHD	Coronary Heart Disease
CID	Charge Injection Device
CMOS	Complementary Metal Oxide Semiconductor
COIL	Chemical Oxygen Iodine Laser
COSY	Correlation Spectroscopy Experiment
CRADA	Cooperative Research and Development Agreement
CSD	Carnahan-Starling-Desantis Equation of State
CSDM	Carnahan-Starling-Desantis-Morrison Equation of State
CRP	Cyclic AMP Receptor Protein
CRT	Cathode Ray Tube
CVD	Chemical Vapor Deposition
dB	Decibels
DC	Direct Current
DHF	Dirac-Hartree-Fock
DLS	Dynamic Light Scattering
DMP	Dimethylphenanthrene
dL	Deciliter (10^{-1} liters)
DNA	Deoxyribonuclei Acid
DP	Differential-pressure Cell
DSC	Differential Scanning Calorimetry
DTSA	Desktop Spectrum Analyzer
ECP	Effective Core Potentials
EDTA	Ethylene-diamine-tetra-acetic Acid
ELISA	Enzyme Linked Immunosorbant Assay
EMPA	Electron Probe X-ray Microanalysis
FAB	Fast Atom Bombardment
FB	Fluidized Bed
FE-STEM	Field Emission-scanning Transmission Electron Microscope
FIIA	Flow Injection Immunoassay
FIAS	Flow-injection Analysis System
FTIR	Fourier Transform Infrared Spectroscopy
FTS	Fourier Transform Spectrometer
FWHM	Full-width, Half-maximum
FY	Fiscal Year. The Fiscal Year Ends on September 30 of the the Specified Year.
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GD	Glow Discharge
HCFC	Hydrochlorofluorocarbon

HFC	Hydrofluorocarbon
HPLC	High Performance Liquid Chromatography
HTPRT	High Temperature Platinum Resistance Thermometer
HTSPRT	High Temperature Standard Platinum Resistance Thermometer
IC	Internal Combustion
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IgG	ImmunoglobulinG
INAA	Instrumental Neutron Activation Analysis
IPRT	Industrial Platinum Resistance Thermometer
IPTS-68	International Practical Temperature Scale of 1968
ITS-90	International Temperature Scale of 1990
LC	Liquid Chromatography
LDV	Laser Doppler Velocimetry
LEI	Laser-enhanced Ionization
LH ₂	Liquid Hydrogen
LIF	Laser Induced Fluorescence
LIMS	Laboratory Information Management System
LOD	Limit of Detection
LOX	Liquid Oxygen
Lp(a)	Lipoprotein (a)
MAP	Measurement Assurance Program
MBWR	Modified Benedict-Webb-Rubin Equation of State
MDL	Minimum Detectable Limit
MECE	Micellar Electrokinetic Capillary Electrophoresis
mg	Milligram (10 ⁻³ grams)
mL	Milliliter
mM	Millimolar (10 ⁻³ molar)
MMA	Monomer Methyl Methacrylate
MOCVD	Metal-Organic Chemical Vapor Deposition
MPI	Methylphenanthrene Concentration Ratios
MS	Mass Spectrometry
MSEL	Materials Science & Engineering
mW	Milliwatt
MW	Molecular Weight
NADH	Nicotinamide Adenine Dinucleotide
NDP	Neutron Depth Profiling
NLS	National Launch System
NMOC	Non-methane Organic Compound
NMR	Nuclear Magnetic Resonance
NSRDS-NBS	National Standard Reference Data - National Bureau of Standards

NTRM	NIST Traceable Reference Materials
OES	Optical Emission Spectrometry
PC	Personal Computer
PCB	Polychlorinated Biphenyl
PCR	Polymerase Chain Reaction
PEELS	Parallel Detection Electron Energy Loss Spectrometry
PFSA	Polyperfluorosulfonic Acid
PGAA	Prompt Gamma Activation Analysis
PLM	Polarized Light Microscopy
PMMA	Poly-Methyl Methacrylate
PPA	Partial Pressure Analyzer
ppb	Parts-Per-Billion
pptr	Parts-Per-Trillion
PVT	Pressure-volume-temperature
PVTx	Pressure-volume-temperature-composition
Rabc	Refrigerant abc
REMPI	Resonance-enhanced Multiphoton Ionization
RF	Radio Frequency
RFLP	Restriction Fragment Length Polymorphism
RIA	Radio Immunoassay
RIMS	Resonance Ionization Mass Spectrometry
RIRT	Rhodium/Iron Resistance Thermometer
RNAA	Radiochemical Neutron Activation Analysis
RSD	Relative Standard Deviation
SAM	Self-Assembled Monolayers
SFE	Supercritical Fluid Extraction
SI	Semi-insulating
SIMS	Secondary Ion Mass Spectrometry
SLM	Standard Laboratory Module
SPRT	Standard Platinum Resistance Thermometer
SRD	Standard Reference Data/Database
SRG	Spinning Rotor Gage
SRM	Standard Reference Material
SSME	Space Shuttle Main Engines
STM	Scanning Tunnelling Microscope
TANGL	Thermoacoustic National Gas Liquefier
TBL	Turbulent Boundary Layer
TC	Thermocouple
TDLAS	Tunable Diode Laser Absorption Spectroscopy
TFTC	Thin Film Thermocouple
THAF	Thermally Assisted Laser Induced Fluorescence
THERM/EST	Thermodynamic Data Estimation
TIMS	Thermal Ionization Mass Spectrometry

TIR	Total Internal Reflection (Spectroscopy)
TLD	Thermal Luminescence Dosimetry
TOF-SIMS	Time-of-flight Secondary Ion Mass Spectrometer
TQM	Total Quality Management
TSC	Test Station Controller
TTB	Technology Test Bed
UIM	Ultrasonic Interferometer Manometer
UNIX	Multitasking Operating System
UV/VIS	Ultra-violet Visible Spectroscopy
VOC	Volatile Organic Compounds
VRD	Video Radiation Detector
WDS	Wavelength-Dispersive X-ray Spectrometry
XRF	X-ray Fluorescence
XPS	X-ray Photoelectron Spectroscopy

